AN EXPERIMENTAL STUDY OF OIL RECOVERY FROM CARBONATE RESERVOIRS BY IN-SITU GENERATED CO_2

BY

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A Thesis Presented to the

DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

PETROLEUM ENGINEERING

December, 2014

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

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I dedicate my work to my parents, brother and sisters who have been supporting to me in all my endeavors.

ACKNOWLEDGMENTS

I would like to express my appreciation and sincere gratitude to thesis committee members Dr. Mohamed Mahmoud, Dr. Sidqi Abu Khamsin and Dr. Abdullah S. Sultan for their continuous support all through my study period. I especially acknowledge the support of Dr. Mohamed Mahmoud. His precious guidance and inspiration helped me grow confidence and develop both academically and personally.

I would like to express my deepest appreciation to Mr. Abdulrahim Mahmoud Muhammadain and Mr. Abdul Samad, who has shown the attitude and the substance of genius, they taught me experimental procedures and implementation with a matter of ease.

I would like to thank my family for their strong support and encouragement throughout my study period.

Special thanks are due to the Department of Petroleum Engineering at King Fahd University of Petroleum & Minerals, including Faculty, Staff and Fellow Graduate Students who contributed directly or indirectly to the accomplishments of this work.

At the end, I am so grateful to all my friends at KFUPM especially Mohammad Danish Hashmat, Sarmad Zafar, Saad Mehmood, Zaeem Hassan, Mobeen Murtaza, and Zaid Zaffar.

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LIST OF ABBREVIATIONS

List of Abbreviations are as follows

MMP	:	Minimum Miscible Pressure
MINSS	:	Minimum Solvent Saturation
GOC	:	Gas Oil Contact
BHP	:	Bottom Hole Pressure
GOR	:	Gas Oil Ratio
WCUT	:	Water Cut
STO	:	Stock Tank Oil
HTHP	:	High Temperature High Pressure
IFT	:	Interfacial Tension

ABSTRACT

Full Name : Muhammad Mansoor Alam

Thesis Title : An Experimental Study of Oil Recovery from Carbonate Reservoirs by In-Situ Generated CO_2

Major Field : Petroleum Engineering

Date of Degree : December, 2014

CO_2 EOR has been widely used in the past because of its advantages (high solubility in oil, reduces viscosity, causes oil swelling, provides high mobility and increases oil recovery). But along with the benefits there are problems of reservoir heterogeneity that include gravity override, viscous fingering, and CO_2 channeling that causes early gas break through and results in reduction in sweep efficiency and ultimately decrease in oil recovery. In this work we present the concept of in-situ CO_2 generation that will cause oil viscosity to reduce, increase mobility of oil and increased sweep efficiency can be achieved when we flood it with water. Citric acid was used to generate in-situ CO_2.

In this work six core flooding experiments were conducted, four of which were done with different concentration of citric acid (2wt%, 5wt%, 7.5wt%, 10wt %), fifth with encapsulated citric acid while the sixth was done with spent citric acid. All experiments were conducted at 100^oC and 1100 psi. Citric acid produces CO_2 in-situ along with calcium citrate as the bi-product which causes the IFT reduction and this IFT reduction adds to the oil recovery mechanism. Core flooding experiment started with sea water flooding followed by citric acid injection and again sea water.

The core flooding experiments gave us increased recovery factor of 59.9, 52.42, 74.05, 83.8, and 84 from 2wt%, 5wt%, 7.5wt%, 10wt% of citric acid and 10wt% of encapsulated citric acid concentrations respectively. The experiment done with spent citric acid resulted in 8% more recovery then sea water confirming IFT reduction due to calcium citrate. The use of in-situ generation of CO_2 resulted in high amount oil recovery dealing effectively with the problems of CO_2 EOR, thus making it potential EOR method.

CMG simulations results concluded that CO_2 injected at residual oil saturation case gave better results when injected into the reservoir and followed by water flooding into the aquifer.

ARABIC ABSTRACT

ملخص الرسالة

الاسم الكامل : محمد منصور علم

عنوان الرسالة: دراسة تجريبية لإستخراج النفط من الخزانات الكربونية عن طريق الإنتاج الموضعي لغاز ثاني أكسيد الكربون

التخصص:هندسة النفط

تاريخ الدرجة العلمية: ديسمبر , 2014

تحسين إنتاج النفط عن طريق إستخدام ثاني أكسيد الكربون كان و مازال يستخدم على نطاق واسع , بسبب مزاياه العديدة (الذوبانية العالية في النفط, تقليل اللزوجة , يؤدي الى انتفاخ النفط, يعطي حركية عالية و من ثمَّ يحسن استخراج النفط). لكن معا هذه المزايا هنالك العديد من المشاكل المتعلقة بعدم تجانس المكمن و التي تشمل تخطيه للنفط نتيجة للجاذبية الارضية , الاصابع اللزجة(سريان الغاز على شكل اصابع داخل النفط) و تسرب الغاز من خلال الشقوق الصخرية, مما يؤدي الى اختراق الغاز المبكر الى آبار الإنتاج ونقصان كفاءة دفع الغاز للنفط و هذا يؤدي في نهاية المطاف الي إنخفاض كمية النفط المستخرجة. في هذا العمل ، نحن نقدم فكرة الإنتاج الموضعي لثاني اكسيد الكربون و التي سوف تؤدي الى تخفيض لزوجة النفط ، زيادة حركية النفط، و تحسين دفع الغاز للنفط عن طريق إستخدام الماء. تم إستخدام حمض الستريك لإنتاج ثاني أكسيد الكربون موضعيا.

في هذا الدراسة تم إجراء ست تجارب لإزاحة النفط عن طريق الماء,تم إستخدام حمض الستريك المخفف (2%، 5%، 7.5% , و 10% تركيز وزني) في اربع من هذه التجارب, و تم إستخدام حمض الستريك المغلف و حمض الستريك المستهلك في التجربتين الخامسة و السادسة على التوالي. تم إجراء كل التجارب عند درجة حرارة 100 درجة مئوية و ضغط 1100 رطل/بوصة مربعة. يقوم حمض الستريك بإنتاج ثاني أكسيد الكربون موضعيا و سترات

الكالسيوم كمنتج ثانوي و الذي يؤدي الى تقليل التوتر السطحي و من ثمَّ تحسين إستخراج النفط. في البدء تم إستخدام مياه البحرلإزاحة النفط وتبعها حقن حمض الستريك ومياه البحر مرة ثانية للتحكم في دفع الحامض.

تجارب إزاحة الماء للنفط أعطت زيادة في كفاءة الإستخلاص النفطي كما يلي: 59.9, 52.42, 74.05، 83.8 و 84 عن طريق إستخدام 2%، 5%، 7.5% , 10% تركيز وزني من حمض الستريك و 10% تركيز وزني من حمض الستريك المغلف على التوالي. إستخدام حمض الستريك المستهلك أدى إلى زيادة إستخلاص النفط بحوالي 8% مقارنة مع إستخدام ماء البحر, و هذا يؤكد على إنخفاض التوتر السطحي نتيجة تكون سترات الكالسيوم. إستخدام الإنتاج الموضعي لثاني أكسيد الكربون أدى إلى زيادة كبيرة في كمية النفط المستخلص كذلك أدى للتعامل بفعالية مع مشاكل تحسين إنتاج النفط عن طريق إستخدام ثاني أكسيد الكربون, و من ثمَّ يمكن إعتبارها إحدى الطرق الفعالة لتحسين إستخراج النفط .

نتائج المحاكاة المكمنية عن إستخدام طريق برنامج سي إم جي أسفرت عن الأتي: حقن ثاني أكسيد الكربون عند التشبع الحرج للنفط يؤدي إلى نتائج أفضل عندما يتم حقن الماء للتحكم في دفع ثاني أكسيد الكربون .

CHAPTER 1

INTRODUCTION

1.1 Overview

The use of CO_2 in EOR and CO_2 sequestration is quite familiar now. Due to the greenhouse effect of CO_2 as a two way task to recover more oil as well as to reduce the CO_2 from atmosphere, the enhanced oil recovery from CO_2 injection is already going on from few decades. CO_2 injection for oil recovery is now a well-developed mechanism and already a lot of oil has been recovered from it.

The purpose of EOR is to recover the oil left behind after the primary and secondary recovery methods. The EOR methods include chemical, gas injection like CO_2, N_2 or hydrocarbons and also the thermal recovery methods. Thermal recovery is done by injecting heat by some hot gas or water. The screening method based on fluid and rock properties. CO_2 is good for several reasons like lower miscibility pressure, better solvent properties, CO_2 sequestration, swelling and lowering viscosity of oil. The increase in the oil recovery by CO_2 injection is achieved by maintaining or increasing reservoir pressure, and replacing the interfacial forces between oil and CO_2.

To understand the concept of oil recovery by gas injection, knowledge of gas miscibility is needed. The term “miscibility” is referred to the ability of two or more fluids (CO_2 and oil here) to form a single phase when they are mixed at any proportion. In a miscible mixing

process one important aspect is the interface elimination between the two fluids. If there is any interface formed at some proportions of one fluid in the other then fluids are termed as ‘‘immiscible’’. In petroleum reservoirs fluids that are miscible with the reservoir fluid, like CO_2, in any proportion are called first-contact miscible fluids. They form a single phase with the reservoir fluid. An injection gas which is not first-contact miscible with the reservoir oil can be made miscible (for certain compositions only) with the reservoir oil by a process known as multiple-contact or dynamic miscibility. This process can be either the vaporizing gas drive (injection gas can extract or vaporize the intermediate components from reservoir oil) or the condensing gas drive (the reservoir oil at the mixing front is made richer by condensing the intermediates from the injected solvent into the oil).

In-situ generation of CO_2 is not new and several investigations were conducted. Shiau et al. (2010) studied compounds that generate CO_2 in-situ. Xiaofei et al. (2013) generated in-situ CO_2 using active acid, polymer and surfactant. Mahmoud et al. (2014) US Patent used HEDTA chelating agents at low pH to generate CO_2 in-situ in carbonate cores. Details will be discussed in section 2.15.

1.2 Need for This Research

As evident from the literature, CO_2 flooding has been widely used to recover as much as oil that could be recovered from the reservoirs. For CO_2 foaming there are problems of foam stability under high saline environment that are usually present in carbonate reservoirs. Foam at this high saline environment may not form and further instability of foam and high mobility of CO_2 cannot be tackled properly. Effectiveness of foam is also reduced by the adsorption of surfactant at the rock surface. In this work we are going to

use in-situ generated CO_2 to recover oil from carbonate reservoirs by injecting low reactive fluid into the reservoir.

Few patents that are discussed later in the literature showed the in-situ generation of CO_2 as a potential method for oil recovery. In this work we will use citric acid to react with carbonate rocks to produce CO_2 in-situ. The purpose of CO_2 generation is to mix with the oil and reduce its viscosity and cause swelling of oil and then we will water flood it after CO_2 generation. The generated CO_2 will reduce the oil viscosity and increase the mobility of oil.

The purpose of this study is to identify the amount of oil that can be recovered from carbonate reservoirs using the in-situ generation of CO_2. IFT (interfacial tension) measurements will be conducted in order to get the idea of IFT reduction and then we will compare the IFT results of sea water to the spent citric acid solution prepared in sea water at different concentrations of citric acid. These concentrations are 2, 5, 7.5, and 10wt% citric acid prepared in sea water. IFT reduction will be an additional advantage as it will cause some additional oil to be produced.

Finally CMG simulation will be used in large scale to validate the concept of in-situ CO_2 generation by injecting CO_2 at the bottom of the aquifer and allow CO_2 to be released in the oil zone and then water flood the swelled oil.

1.3 Problem Statement

For CO_2 foaming there are problems of foam stability under high saline environment that are usually present in carbonate reservoirs. Foam at high saline environment may not form and further instability of foam and high mobility of CO_2 cannot be tackled properly.

Effectiveness of foam is also reduced by the adsorption of surfactant at the rock surface. Also CO_2 has the problem of gravity override when injected in thick reservoirs, the in-situ CO_2 generation will solve these problems. In this research we will generate CO_2 in-situ to eliminate displacement efficiency problems such as gravity override and foam quality.

1.4 Thesis Objectives

The purpose of this study is to study the amount of oil that can be recovered using in-situ generation of CO_2 in carbonate reservoirs using citric acid at different forms and concentrations. Also CMG will be used to validate this concept in large scale by injecting CO_2 into the aquifer and allow it to slow release to the oil zone, then followed by water flooding.

1.5 Thesis Organization

This thesis has been prepared according to the instructions specified by the Deanship of Graduate Studies of King Fahd University of Petroleum & Mineral. It has been divided into six chapters as follows;

Chapter 1: Introduction.

Chapter 2: explains the literature review which covers the basics of CO_2 flooding.

Chapter 3: experimental part.

Chapter 4: Results and Discussion.

Chapter 5: Conclusion and Recommendations.

CHAPTER 2

LITERATURE REVIEW

The literature review discusses use of CO_2 in different methods and mechanisms. Later in this chapter literature review of in-situ generated CO_2 will be discussed.

2.1 Foam in Porous Media

Foam formed in porous media is the dispersion of gas in liquid so that gas phase is interconnected with liquid phase causing blockage in few gas flow paths by lamellae Falls et al. (1988). Three flow regimes are encountered in the study of foam in the field:

(1) During the inertial flow bulk of foam can be created at the well and further extended to surface facilities.

(2) The regions of high differential pressure (ΔP) and high flow rates such as near the wellbore and rock face region.

(3) The region after the injection well, i.e. regions where there are low ΔP and low flow rates Rossen, (1995).

All the above flow regimes have different flow behavior and mechanisms of foam generation. Further focus of study will be on the third flow regime, as shear forces are low and pore-scale displacements are carried out by capillary forces not by viscous forces.

2.2 Foam Generation Mechanisms

1) As the gas invades from one pore to adjacent pore throat stabilized liquid films or lenses are created that are termed as “leave behind”, as shown in Fig.2-1. It is sometimes termed as less effective mechanism even than it creates a good quantity of lamellae but if “leave behind” is the only mechanism responsible for lamellae creation the gas will flow in one continuous path.

2) When a single lamella is divided into two which occurs as a result of flowing lamellae passing through a pore or a gap that has one or more throats resulting in breaking or spanning both open pore throats, is termed as “Lamella division”, as shown in Fig.2-2.

When lamellae are created in pore throats filled with gas, if the local capillary pressure decreases by half of entry pressure of the throat, and it will depend upon the pore throat geometry and medium wettability, this mechanism is termed as “Snap-off”. For three dimensional (3D) pore geometries, the values of one-half represent reasonable value (Chen M. et al. 2006).

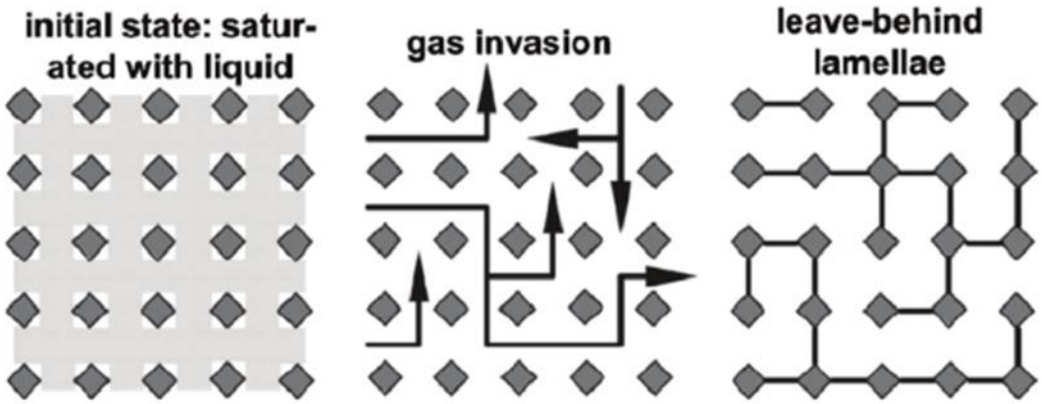


Figure 2-1: leave behind mechanism, Gray squares are sand grains and gap between them are pore and pore throats. (Chen M. et al. 2006).

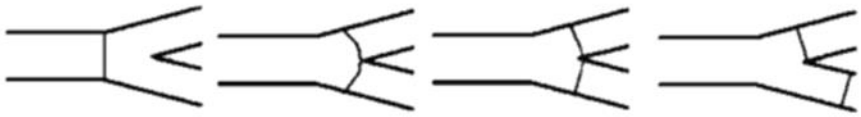


Figure 2-2: Here in first two panels, lamellae enters branching point (pore body). And in last two panels, lamellae dividing in to two downstream throats, thus one additional lamellae is created. (Chen M. et al. 2006).

Figure 2-3: Blacks shown are pore-throat wall, gray are water, and whites are gas (Chen M. et al. 2006).

2.3 Foam Termination Mechanisms

When oil is not present, lamellae breaks in porous media by the following mechanisms:

1) Capillary Suction Coalescence: When lamellae are in movement they coalesce due to rapid stretching in large pore bodies. For the given combination of capillary pressure and gas flow rate, pore body and pore throat having large aspect ratios are the cause of foam termination sites. And when the capillary pressure of the medium or the gas velocity increases, we get more combinations of pore throat/pore body termination sites.
2) Gas diffusion Coalescence: Those that are in bubbles, in rest or trapped are terminated by different mechanism. When two bubbles having different curvatures come into contact, diffusion of gas takes place from highly curved (smaller bubbles) to less curved (bigger bubbles) through the lamellae in contact. As a result smaller bubble will become part of the common lamellae. Chambers and Radke, (1990).

As discussed above, both mechanisms will result in forming one big bubble in the pore body instead of two smaller bubbles occupied initially. The first mechanisms occur by a fast physical phenomenon while second is result of slow diffusion process.

2.4 Mechanisms of Foam Destabilization by Oil

Oil can destabilize foam by different mechanisms but every type of oil does not degrade all the foams. Surfactants that produce foam may be absorbed by oil due to which surfactants at the interface of gas/liquid and aqueous phase will deplete or lamellae may also absorb the surfactants, due to which less amount of foam will form. For commercial

foam forming, above discussed changes in phase-behavior are negligible for light crude oil/foam forming surfactants condition and combination (Schramm & Novosad, 1990). Foam destabilization depends on the oil composition and its components. Some researchers have reported that light crude oil degrades more foam as compared to heavy oil (Schramm & Novosad, 1992) and (Schramm, Turta, Novosad, & Inst, 1993). Spreading of oil on foam lamellae spontaneously and displacing the elastic stabilizing interface or the spontaneous emulsification of oil may take place, due to which oil may enter stabilizing interface. Usually the mechanisms with physical phase change are considered important (Schramm & Novosad, 1990).

2.5 Pore Scale Displacement Mechanisms of Foam

With multi pore level, high permeability regions are filled with bubbles initially in the micro model and then proceed towards the regions of low permeability and dead pores which will contain more residual oil after water flooding. But with single pore level, other oil displacement mechanisms are involved which will contribute and enhance oil production (Emadi et al. 2011). Following are the four mechanisms reported in the literature. The mechanisms are reported and listed on the basis of time when they appear in micro model.

1) Direct Displacement: Direct displacement occurs either by the aqueous phase or CO_2 bubbles. Heavy oil displacement by CO_2 bubbles is more effective as compared to CO_2 flood taking place by double drainage process. And this is because of the fact that every single bubble of foam is a new CO_2 front and it is not necessary that they follow each other to lead more effective flooding. Pore blockage

from bubbles of foam decrease the permeability of gas and also cause flow restriction in the aqueous phase path due to this restriction, surfactant solution flows into other pore space.

2) Emulsification of oil: After the initial direct displacement, the residual oil saturation was again high. With further CO_2-foam injection displacement of large amount of residual oil took place and flowed to the end of micro model in the form of water emulsion of oil (droplets form) formed in between bubbles of CO_2 foam. These emulsions remained stable till the end of the micro model due to presence of the surfactant material in aqueous phase. Due to lower apparent viscosity of these oils in the form of water emulsion compared to heavy oil, results in improved oil displacement. Fig.2-4 shows magnified micro model section we can clearly see the flow of water oil emulsion in between CO_2 bubbles. Arrow directions denote the flow of oil emulsions. Formation of oil emulsion is well known and well discussed phenomenon in the literature (Yang and Reed, 1989; Kuhlman, 1990).

3) Co-current film flow: As CO_2 bubbles were occupying the center of the pore, residual-oil remained connected to the oil films on pore walls or occupied in between the foam bubbles. Therefore as foam flow is continued the residual oil was produced through these oil films. Residual oil production continued with the foam flow. Displacement became more effective because of the parameters like non-Newtonian nature, high viscosity of CO_2 foam and high number of interfaces between CO_2 bubbles. Magnified sections in the Fig.2-5 below shows micro model

in which we can clearly see oil films on the pore walls and in between foam bubbles. Later these layers of oil were remobilized and displaced in the same flowing direction as CO_2 foam.

4) Counter-current film flow: The above mentioned film flow occurs in the interconnected pores, residual oil was also recovered from dead end pores but in a different manner. In which CO_2 bubbles occupied the center of the pores and forced resident oil out from oil layers around CO_2 bubble in the opposite direction. But this displacement from dead end pores was slower than the emulsification mechanisms and co-current film flow from interconnected pores. Fig.2-6 shows series of residual oil production from dead-end pores by the co-current (counter current) film flow mechanism.

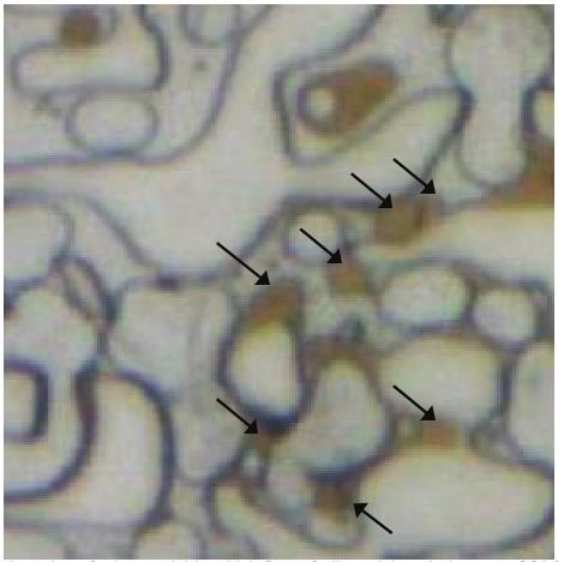


Figure 2-4: Magnified section of micro model, we can clearly see the flow of water oil emulsion in between CO_2 bubbles (Alireza Emadi et al. 2011).

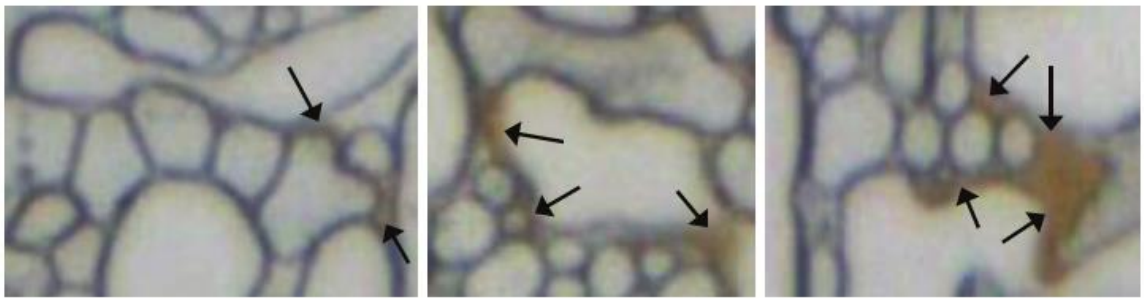


Figure 2-5: Magnified sections of micro model with oil films as brown arrows in between CO_2 bubbles: CO_2 bubbles and pore walls (Alireza Emadi et al. 2011).

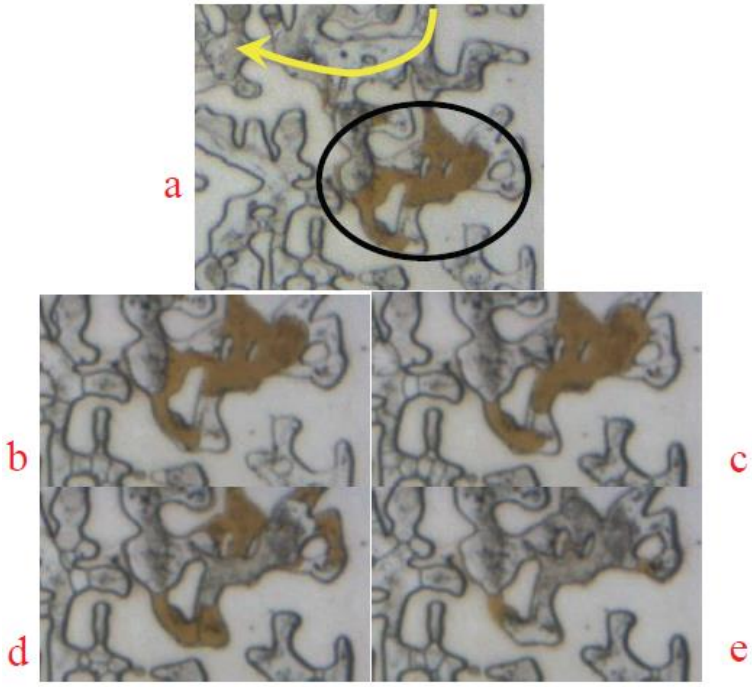


Figure 2-6 Magnified section of the micro model after (a) 1 hour, (b) 1.5 hours, (c), 2 hours, (d) 2.5 hours and (e) 3 hours of simultaneous surfactant/ CO2 injection in test. The series of pictures show foam displacing residual oil from dead end pores and occupy

2.6 Miscible Flooding Criteria

Important factors to decide miscible CO_2 flooding are as follows:

1-For Miscible CO_2 EOR, the most important and critical parameter is the minimum miscibility pressure (MMP), which is function of reservoir properties such as pressure and temperature of reservoir and also the injected CO_2 purity.

2- Second important thing is CO_2 injection rate into the reservoir, which is termed as reservoir injectivity. Also depends on the storage capacity of the reservoir.

3- Geologic heterogeneity will influence the early CO_2 breakthrough and the amount of CO_2 that can be recycled.

The most important criterion in Miscible CO_2 flooding is MMP, for selecting candidate reservoir MMP should be less than the initial reservoir pressure.

Reservoir properties other than MMP that will further help in selecting candidate reservoir includes oil API gravity, oil viscosity, depth of reservoir, reservoir oil saturation, and heterogeneity of reservoir are the most important. Cracoana (1982) suggested an API gravity of greater than 40° and viscosity of oil values less or equal to 1 centipoise (cp). Stalkup (1984) suggested an API gravity of greater than 27° API and depth of reservoir must not be shallower than 2500 ft. Others suggested API oil gravity range between 11 and 30 degrees. MMP controls both of the constraints such as API oil gravity and viscosity. Stalkup (1984) suggested residual oil ranging 20 to 25% saturation which is basically an economic concern.

CO_2 EOR method is applied to the reservoirs that have been produced through water flooding or any other secondary recovery method, at this stage all the easily movable oil is produced and a significant amount of residual oil is left, which is not able to be produced without an EOR method.

2.7 Estimating Minimum Miscibility Pressure

Whether oil is miscible with CO_2 or not is the key criteria to be known to execute an economic CO_2 EOR. Miscibility increases with depth, oil gravity and the pressure increase helps making it miscible with oil. It is possible to determine MMP using available data and empirical equations.

Using two simple steps we can determine MMP. First we determine the C5+ oil components molecular weight, then by using correlation of C5+ molecular weight and oil API gravity by Lasater (1958) can be used as shown in figure below. To determine the same correlation empirically equation (1) can be used.

$$M = (7864.9/G)^{1/1.0386} \quad (1)$$

Where

$$M = C5 + Component\ Moleculerweight$$

$$G = Oil\ API\ Gravity$$

Then, we determine the MMP by molecular weight of C5+ and reservoir temperature.

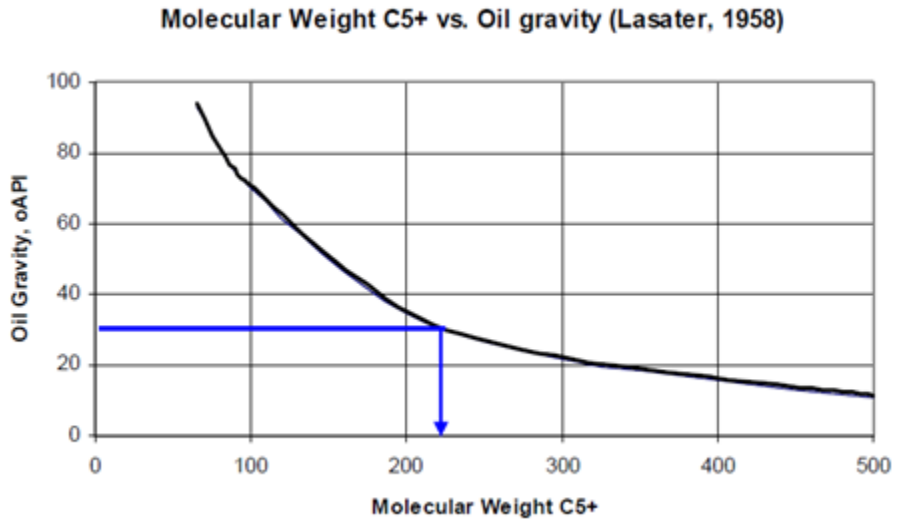


Figure 2-7: Correlation of C5+ oil components molecular weight and oil gravity (Lasater,1958)

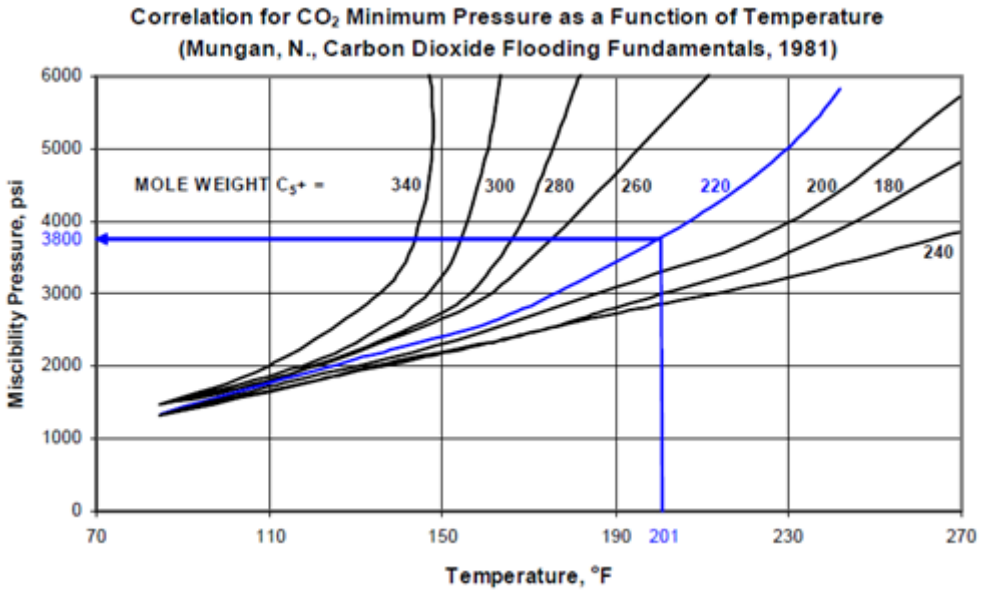


Figure 2-8: Nonlinear relation b/w temperature and Molecular weight of C5+ component of Oil and MMP (Mungan 1981)

To estimate MMP, above relation was developed by multiple non-linear multiple regression

$$MMP = -329.558 + (7.727 * M * 1.005^{T}) - (4.377 * M) \quad (2)$$

2.8 Effect of Pressure on CO_2 Solubility in Brine

CO_2 solubility in formation brine is a strong function of pressure as shown in the Fig.2-9. Brine salinity was 1 mol NaCl/kg and temperature was 323 K. As pressure Increases from 0.1 MPa to 10 MPa, CO_2 solubility rapidly increases then it almost becomes flat though a very sharp increase can be seen as pressure is increased further 1 MPa. Three data points calculated by experiments are shown by black squares.

2.9 Effect of Temperature on CO_2 Solubility in Brine

As temperature increases CO_2 solubility decreases as shown in Fig.2-10. The plot was made using Experimental and simulation data. For Duan et al. Simulation data salinity was taken as 1 mole NaCl/kg and Pressure as 10 MPa. The lowest value measured by Rump et al. (1994) is due to high brine salinity. Plot was made using Duan et al.'s (2003, 2006) data which is simulation data (open diamonds); and all the other points labeled are measured values from experimental.

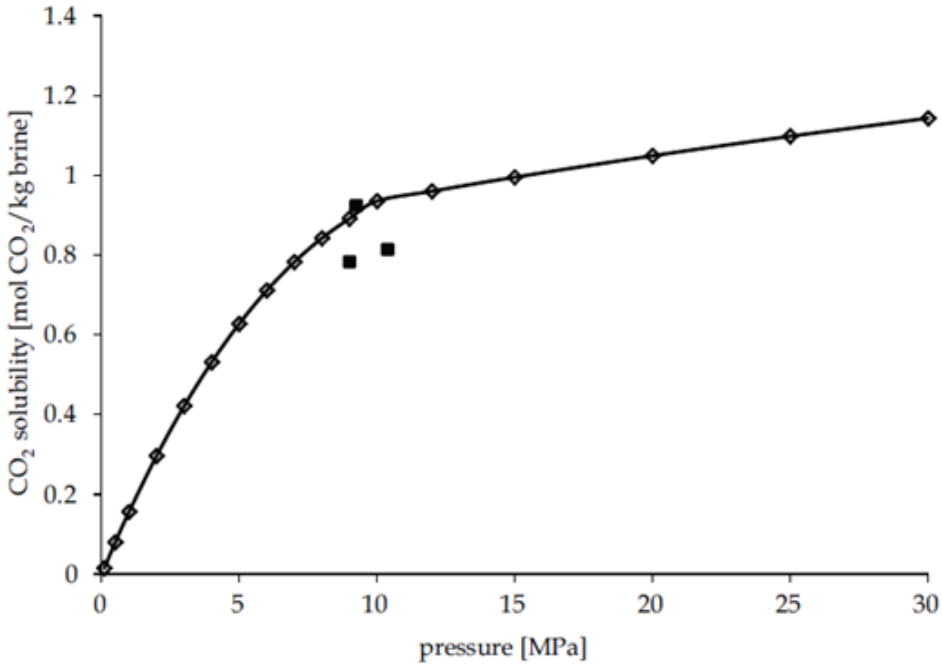


Figure 2-9: CO_2 solubility increases with pressure increase (Duan et al.'s (2003, 2006).

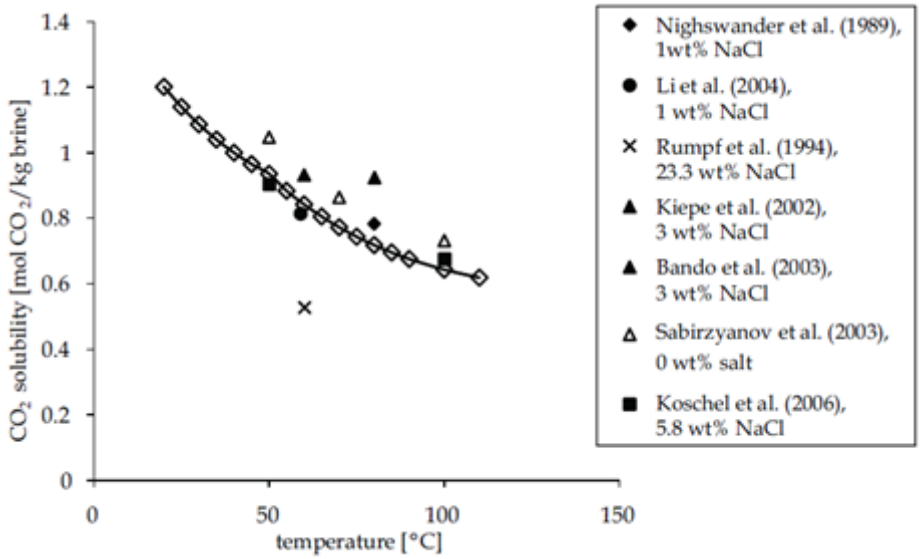


Figure 2-10: CO_2 solubility versus temperature at high pressures (Duan et al.'s (2003,2006).

2.10 Effect of Brine Salinity on CO_2 Solubility in Brines

As salinity increases, CO_2 solubility decreases. Fig.2-11 shows CO_2 solubility vs brine salinity. It also depends on the type of salts dissolved. Yasunishi and Yoshda (1979) worked on measuring the CO_2 solubility at atmospheric pressure using variety of salts, having divalent and trivalent cations with chloride and sulphate. They found that CO_2 is more soluble in KCl as compared to NaCl solution having same electrolytic concentration. While for divalent CO_2 has approximately same solubility for both $CaCl_2$ and $MgCl_2$ solutions. And comparatively, for the same salt concentration of monovalent i.e. NaCl or KCl absorbed more CO_2 than the divalent $CaCl_2$ or $MgCl_2$ for the same salt concentration. Enick and Klara (1990) reported CO_2 solubility effect by salinity for temperature range between 298 to 523 K and pressure ranges 3.40 to 72.41 MPa. They reported an empirical equation (3).

$$Y_{CO_2,brine} = Y_{CO_2,pure\ H2O}\ (1 - 0.04893414.S + 0.001302838.S^2 - 0.00001871199.S^3) \quad (3)$$

Where

$Y_{CO_2,brine}$ = CO_2 solubility in brine (mass fraction)

$Y_{CO_2,pure\ H2O}$ = CO_2 solubility in pure water (mass fraction)

S = salinity of brine (weight percent)

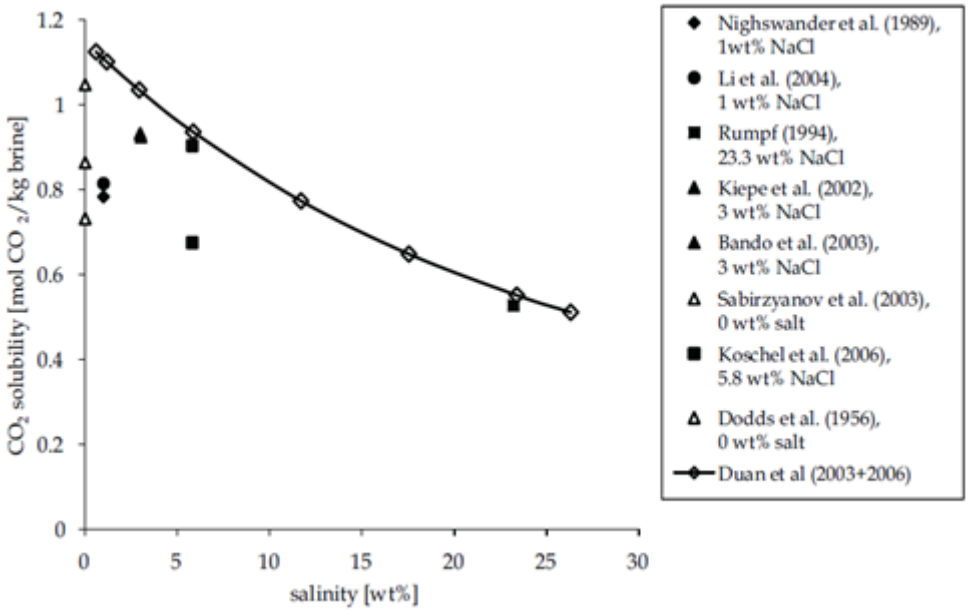


Figure 2-11: CO_2 solubility vs brine salinity. The data used for plotting the curve is from Duan et al. (2003,2006)'s CO_2 solubility calculator; while points labeled on the right also measured from different experiments

2.11 Effect of Injection Depth on CO_2 Solubility

As we go deeper in the oil reservoir or a saline aquifer we encounter high temperature and pressure. The pore pressure is assumed equal to the hydrostatic pressure and hydrostatic pressure gradient is 10.35 MPa/1000m (Dake 2007). And along with it geothermal gradient affect so as we go deeper reservoir temperature increases. Typical geothermal gradients are 25-30 K/1000 m (Fridleifsson et al. 2008). Average values with depth are listed in the table below which is taken form Span and Wagner (1996) and 1 mol/kg NaCl brine, calculated with Duan et al.'s (2003, 2006) calculator.

Table 2-1: Temperature, Pressure, CO_2 solubility and CO_2 density with depth (Duan et al.'s (2003,2006).

Depth (m)	Temperature (K)	Pressure (Mpa)	density (kg/m3)	CO_2 solubility (mol/kg)
0	293	0.1	1.8	0.0307
100	296	1.135	21.8	0.3036
200	299	2.17	43.7	0.5037
300	302	3.205	68.3	0.6496
400	305	4.24	96.5	0.7542
500	308	5.275	130	0.8274
600	311	6.31	171.7	0.8769
700	314	7.345	211.8	0.9082
800	317	8.38	311.8	0.926
900	320	9.415	391.9	0.9338
1000	323	10.45	412.8	0.9353
1100	326	11.485	449.6	0.9344
1200	329	12.52	486.3	0.9334
1300	332	13.555	522.7	0.933
1400	335	14.59	561.3	0.9335
1500	338	15.625	576.1	0.9348

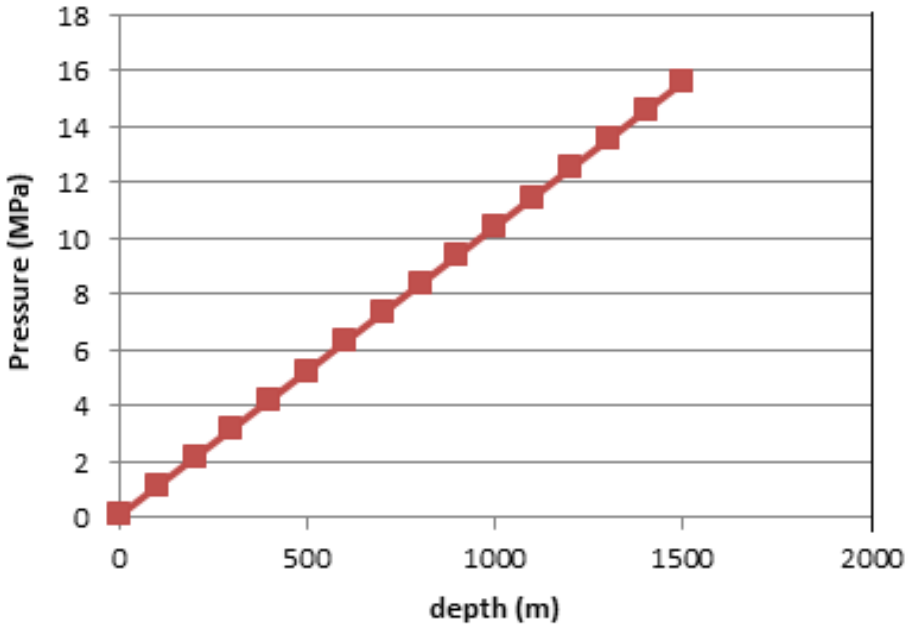


Figure 2-12: Pressure vs depth (Duan et al.'s (2003, 2006).

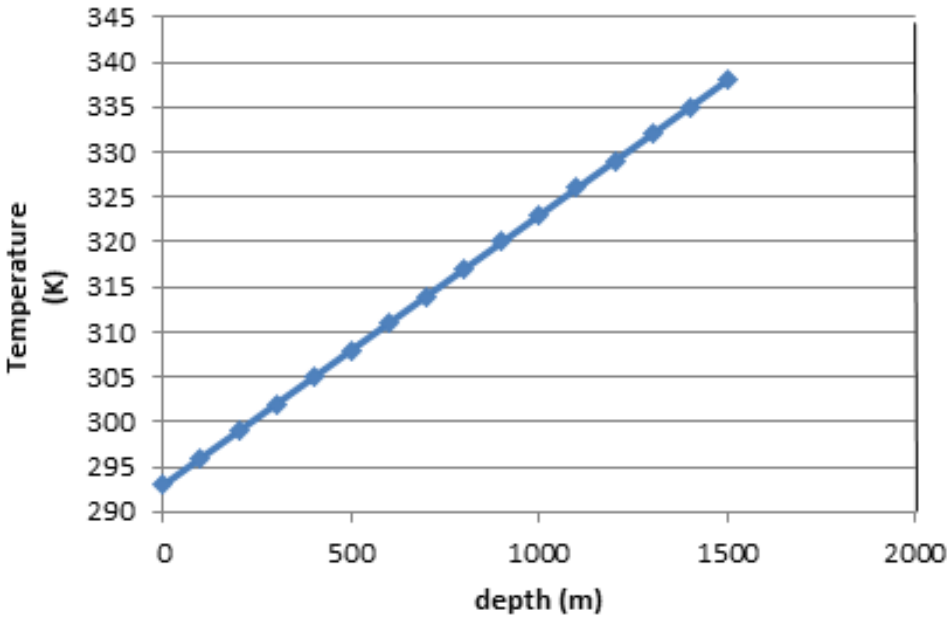


Figure 2-13: Temperature vs depth (Duan et al.'s (2003,2006).

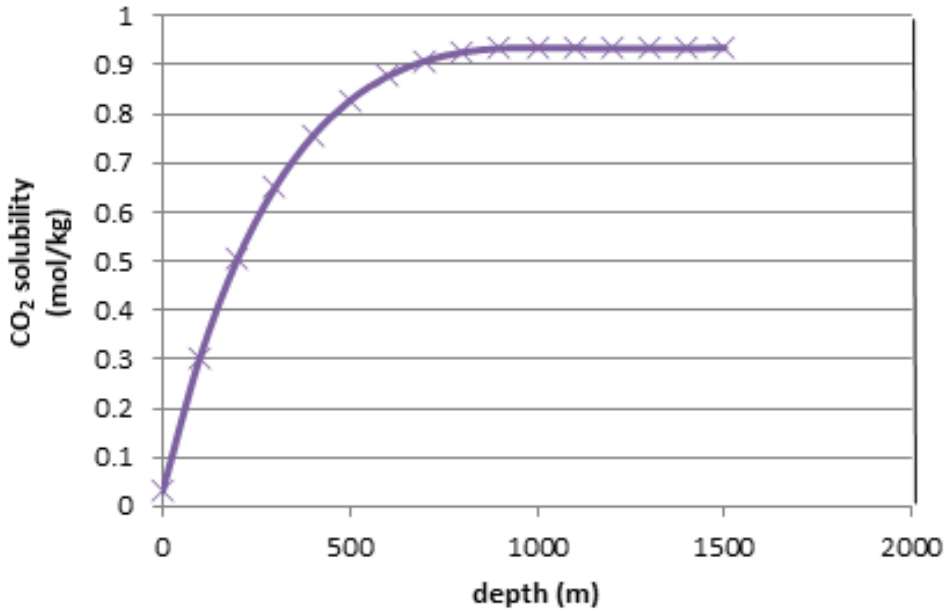


Figure 2-14: CO_2 solubility vs depth (Duan et al.'s (2003,2006).

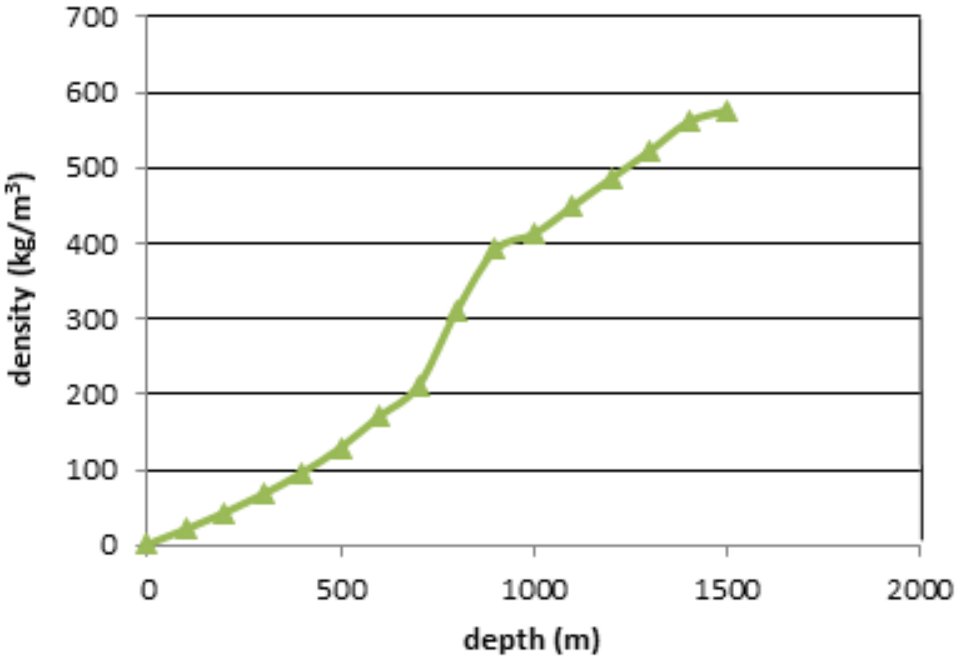


Figure 2-15: Density vs depth (Duan et al.'s (2003,2006).

So as we go deeper temperature increases i.e. CO_2 solubility decreases and pressure increases i.e. CO_2 solubility increases. Therefore pressure and temperature cancel each other effect and CO_2 solubility increases with depth.

2.12 CO_2 Solubility in Oil

CO_2 can dissolve up to 60-80 mol% in oil (De Ruiter et al. 1994, Kokal and Sayegh 1993, Emera and Sarma 2006, Firoozabadi and Cheng 2010). CO_2 solubility in oil increases with pressure and is high at lower temperatures. For temperature below critical temperature of CO_2 (Tc = 304.13 K), CO_2 solubility will increase until it reaches CO_2 liquefaction pressure (5.88 MPa), then it will not increase even if pressure is increased further. Solubility also depends on oil composition and for light crude oil CO_2 can be completely or highly miscible. De Ruiters et al. (1994) reported CO_2 solubility as a function of pressure and it increases with pressure, In his tests he kept lower temperature as (0.69 MPa) for which gas oil ratio was 5.3 m3/m3 approximately and sharp increase was seen in GOR until CO_2 liquefaction pressure was reached, and they got GOR value of 71 m3/m3 and 102 m3/m3, respectively for the two crudes tested. As pressure was increased further GOR almost kept constant, the temperature was kept low at 290K, But if the temperature is above Tc CO_2 solubility increases; but not as much as it increases for lower temperatures (Kokal and Sayegh 1993).

For heavy oils CO_2 gets dissolved into oil phase and few light oil fractions are extracted into the CO_2 phase. It will depend upon the composition of oil and thermo physical condition, vapor-liquid, liquid-liquid-vapor, liquid-supercritical fluid, liquid-liquid are the

different phase behaviors that are seen. The density of oil saturated with CO_2 will increase for lower values of temperature for example 294 K and will decrease as temperature is increased, for example 413 K. (Kokal and Sayegh 1993).

So for tertiary oil recovery CO_2 is a high recovery solvent (Green and Willhite 1998, Blunt et al. 1993). As CO_2 is dissolved in to oil it reduces viscosity of oil due to which mobility ratio of oil and injected fluid increases and high sweep efficiency is achieved. Due to increase or improvement in oil relative permeability flow of oil is improved in the reservoir, and higher oil production is achieved. CO_2 also causes oil swelling (up to 50-60%, Firoozabadi and Cheng 2010) which further enhances oil production.

2.13 Swelling and Fluid Properties of CO_2-Oil Mixtures:

Slim tube tests do not provide fluid properties and phase behavior data which is required for compositional simulation, especially for tuning an equation of state (Fawaz al-Otaibi et. at 2012). For acquiring this data swelling test is performed in batch mode in static PVT cells, in this test, a fixed amount injected gas is allowed to mix with reservoir oil and oil swelling, density, compositions and mixture viscosity are measured. These tests are termed as solubility or swelling tests. The purpose of these tests is to measure the change in properties of oil, as it is mixed with the injected gas and results in reduction of oil density, reduction in oil viscosity and swelling of oil in the reservoir, change in GOR and change in saturation pressure. This test is performed in high temperature-high pressure PVT windowed cell. A known volume of 40 cc reservoir fluid was kept at 5000 psig (this

pressure greater than the reservoir pressure) and reservoir temperature is achieved in the cell by heating. At these conditions, oil density is measured. To determine relative volume, saturation pressure and liquid density a constant composition expansion (CCE) is performed for the original oil. In the experiment pressure is reduced in steps and the volume is recorded for all steps. To prepare first oil-injected gas mixture, a certain amount of gas is injected up to desired mole%. Again by same method CCE is performed to determine relative volume, saturation pressure and liquid density. Same is repeated several times for different mixtures (such as 10, 20, 40 and 60 mole% injected gas). CCE plot is shown in the Fig.2-16 below and swelling data is plotted in Fig.2-17 (Fawaz al-Otaibi et al. 2012).

CO_2 injection reduces the oil viscosity. Viscosity reduction of oil in each step of pore volume injected, using PVT apparatus. A typical viscosity plot for different mixtures is shown in Fig.2-18 (Fawaz al-Otaibi et at, 2012).

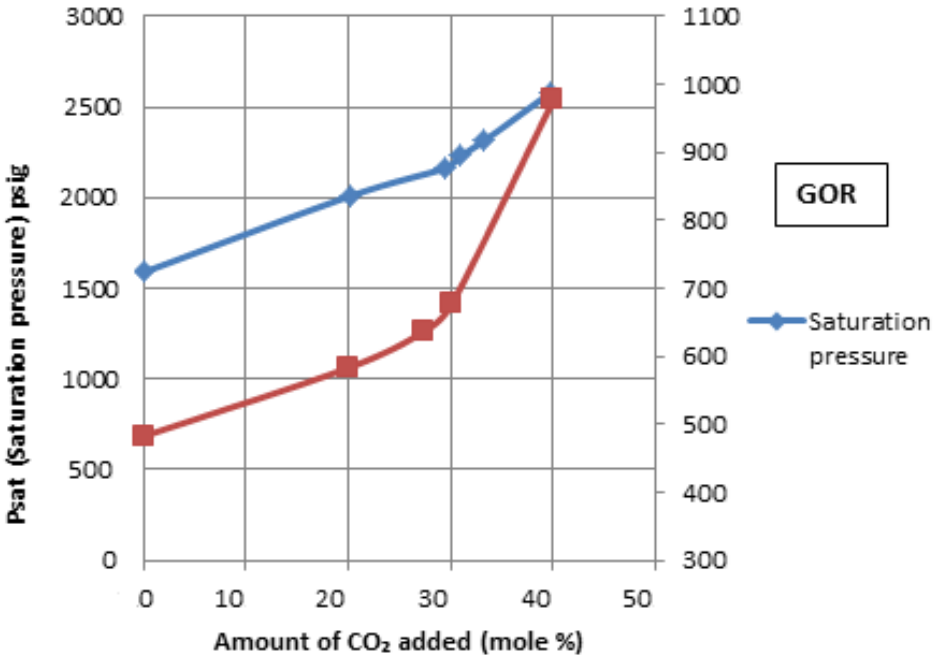


Figure 2-16: Swelling test summary (Saturation Pressure and GOR), (Fawaz al-Otaibi et at, 2012).

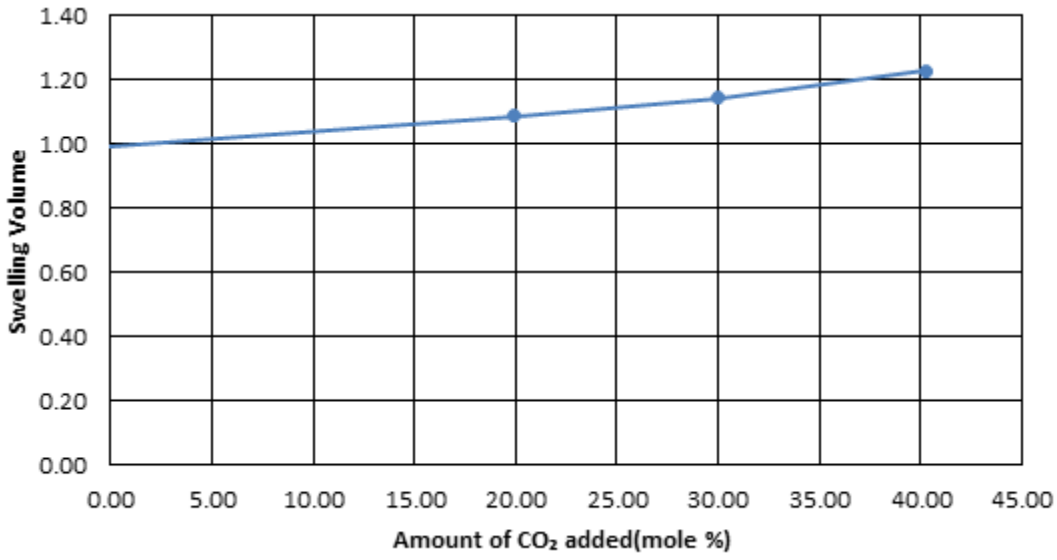


Figure 2-17: Swelling volume versus amount of CO_2 added. (Fawaz al-Otaibi et at, 2012).

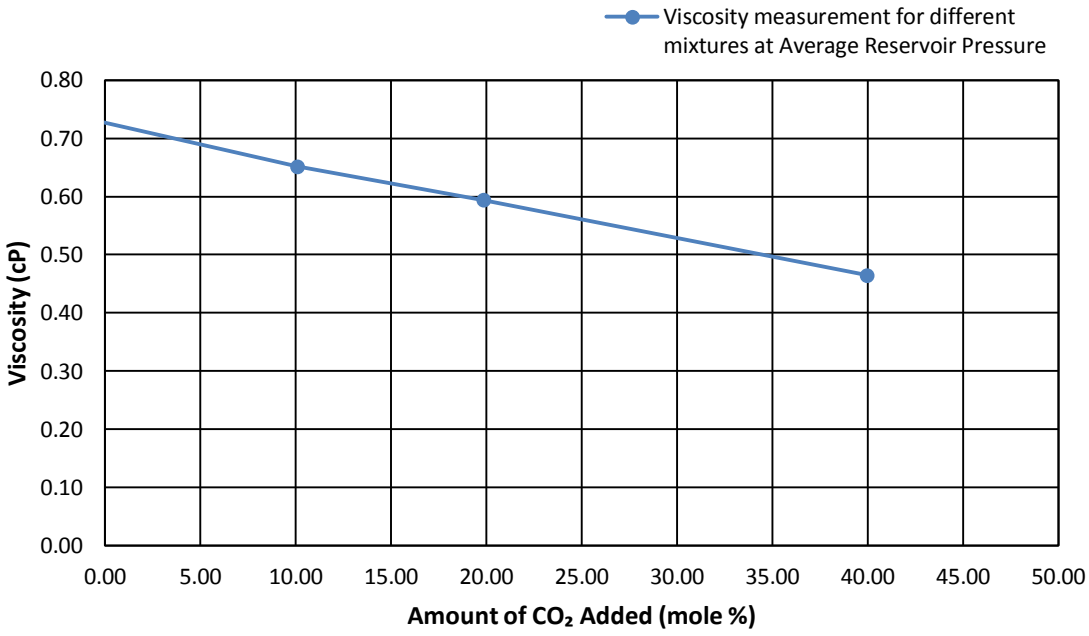


Figure 2-18: Oil viscosity versus amount of CO_2 added (Fawaz al-Otaibi et at, 2012).

2.14 Effect of CO_2 in Oil Viscosity

As CO_2 is highly soluble with in oil, oil viscosity reduces significantly as CO_2 is dissolved in it. D. Brant et al (1993), conducted several experiments to find out oil viscosity reduction under different conditions.

Table 2-2: Change in Oil Viscosity at Pressure = 19 Mpa (D.Brant et al. 1993)

Change in Oil Viscosity at Pressure = 19 Mpa (2755.7163 PSI)				
Oil No	Oil API	Initial Oil Viscosity (cp)	CO_2 Saturated Oil Viscosity(cp)	% Reduction
1	15	953	22	97.6
2	12.4	5660	196	96.5
3	9.6	25022	372	98.5

The magnitude of oil reduction this much high was achieved at 19 MPa, if saturation cut off pressure is as low as 8 MPa, substantial oil viscosity reduction was achieved as follows:

Table 2-3: Change in Oil Viscosity at Pressure = 8 Mpa (D.Brant et al. 1993)

Change in Oil Viscosity at Pressure = 8 Mpa (1160.3016 PSI)				
Oil No	Oil API	Initial Oil Viscosity (cp)	CO_2 Saturated Oil Viscosity (cp)	% Reduction
1	15	953	171	82.1
2	12.4	5660	1743/	69.2
3	9.6	25022	2532	89.6

Table 2-4: Oil with 15 degree API, Measured Physical Properties as a function of CO_2 Concentration (D.Brant et al. 1993)

Temperature=27ºC		Temperature=100ºC			Temperature=175ºC									
CO_2 Sat Pres	**Viscosity**	**Swelling Factor**	**GOR**	**Density**	**CO_2 Sat Pres**	**Viscosity**	**Swelling Factor**	**GOR**	**Density**	**CO_2 Sat Pres**	**Viscosity**	**Swelling Factor**	**GOR**	**Density**
k Pag	(cp)		(m^3/m^3)	(kg/m^3)	k Pag	(cp)		(m^3/m^3)	(kg/m^3)	k Pag	(cp)		(m^3/m3)	(kg/m^3)
4482	953	1	13	947.1	6315	27.2	1	13	922	7239	7	1	13	860.1
5860	834	1.02	17.8	933.6	9860	12.6	1.035	23.2	924	8963	5.2	1.015	21	862
8790	171	1.062	28.8	949.6	12240	11.1	1.071	33.5	924.5	12928	3	1.06	36.4	863
10860	75	1.093	68.6	957.6	16200	8	1.15	65.9	925	15926	2.5	1.12	48	866
13513	30	1.124	84.6	965.9	18270	5.6	1.222	86.8	926	18271	2.4	1.199	57.3	869
16547	22	1.201	98	970										

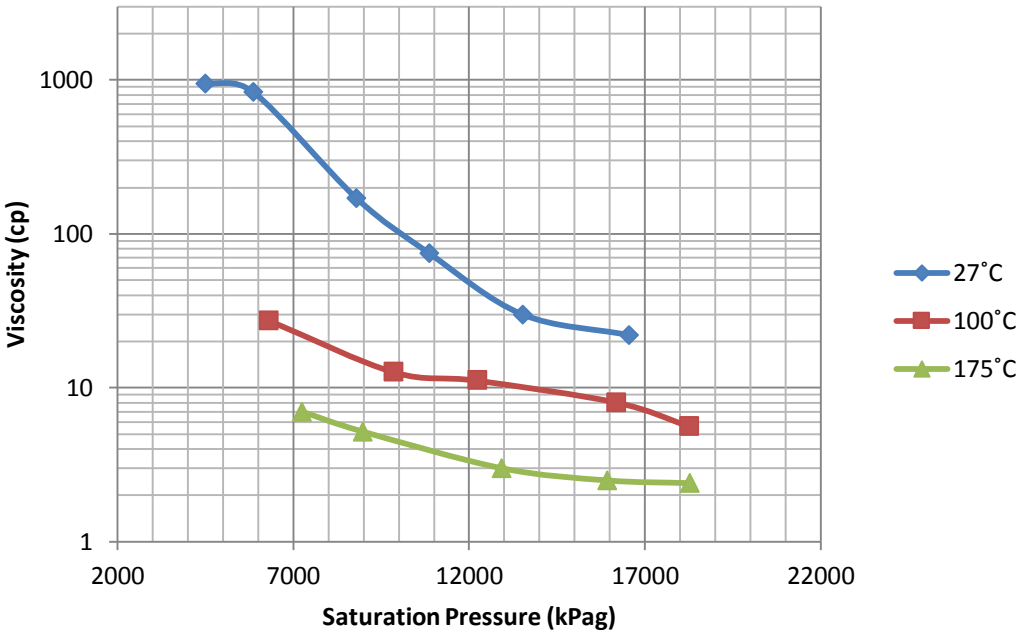


Figure 2-17: Viscosity vs Saturation Pressure (15 ˚API Oil) (D.Brant et al.1993)

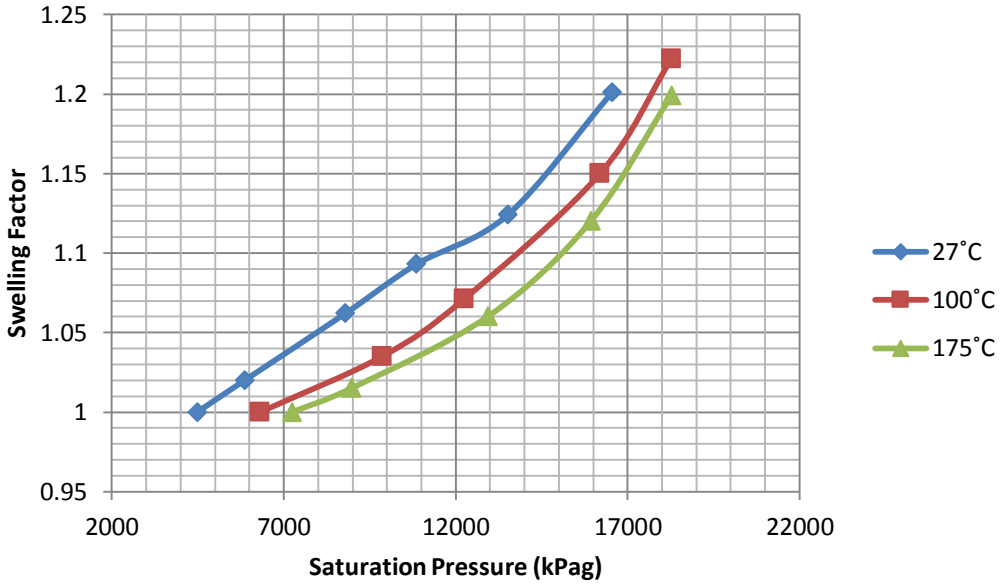


Figure 2-18: Swelling Factor vs Saturation Pressure (15 ˚API Oil) (D.Brant et al. 1993)

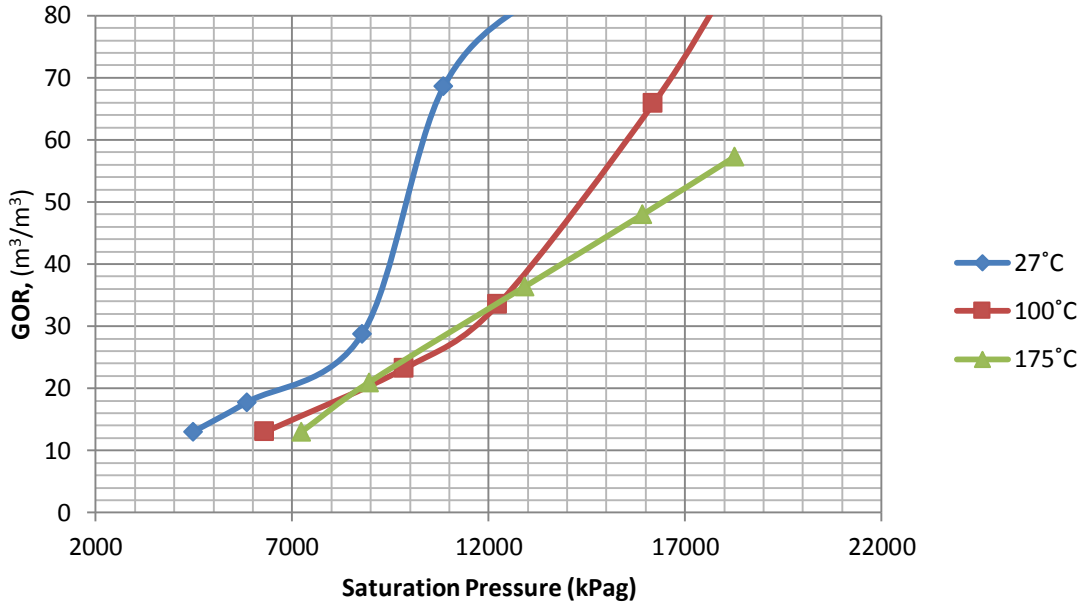


Figure 2-19: GOR vs Saturation Pressure (15 ˚API Oil) (D.Brant et al. 1993)

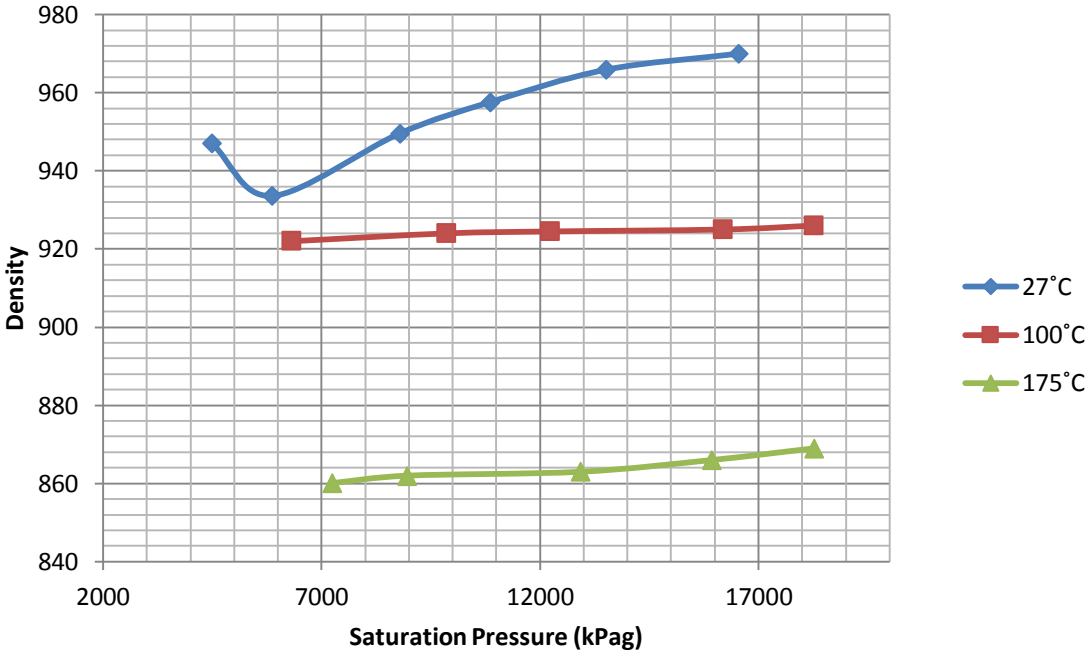


Figure 2-20: Density vs Saturation Pressure (15 ˚API Oil) (D.Brant et al. 1993)

2.15 In-Situ Generation of CO_2

Shiau et al. (2010) investigated compounds that generate CO_2 in situ, ammonium carbamate produce significant amount over heating 85^oC and decreased oil viscosity. Additional ammonium carbamate is used to produce CO_2 at higher temperature. CO_2 measurement is done through combination of acid titration and thermal equipment in which HCl reacts with sample to release CO_2 from material used, and volume of CO_2 is calculated thorough the amount of water displaced in the burette. When comparing polymer/surfactant and polymer/carbamate/surfactant chemical floods, more oil is recovered using the polymer/carbamate/surfactant chemical flood.

Using carbamate in conjunction with a 0.1 PV surfactant chemical flood enhanced crude oil recovery by 5.9% when compared to not using carbamate.

Using carbamate in conjunction with a 0.3 PV surfactant chemical flood enhanced crude oil recovery by 9.7% when compared to not using carbamate.

Using carbamate in conjunction with a surfactant chemical flood enhanced crude oil recovery by 14.1%, when the volume of the surfactant solution was increased from 0.1 PV to 0.3 PV. In all studies the use of carbamate in conjunction with a surfactant chemical flood showed an enhanced crude oil recovery relative to not using carbamate.

Xiaofei et al. (2013) generated CO_2 in-situ using active acid, polymer and surfactant to solve the problem of reservoir heterogeneity and high water to oil viscosity ratio which results in mono layer and mono-directional flow. They carried out lab experiments, generated in-situ CO_2 flooding. CO_2 flooding reduced injection pressure and effectively

plugged channeling between injection-production wells. As a result they were able to achieve, increased Swept Volume, increased oil and decreased water cut.

Phelps et al. (1988) US Patent, minimizing gravity override CO_2 mixed with a polysaccharide gel of a size sufficiently greater than the pores contained in a more permeable formation area is prepared ex-situ in the presence of sodium hydroxide. Said gel is then pumped into said formation causing pores in the more permeable formation area to be blocked off. Thereafter, carbon dioxide flooding is commenced and said flood is directed into the less permeable formation area causing hydro-carbonaceous fluids to be produced there from.

Mahmoud et al. (2014) US Patent used HEDTA chelating agents at low pH to generate CO_2 in-situ in carbonate cores. The in-situ generated CO_2 increased the oil recovery by 35% after sea water injection. The method is particularly for carbonate reservoirs.

2.16 Amount of CO_2 to be used For EOR

Amount of CO_2 that would be used for the additional Oil recovery can be estimated from a quick look method on the basis of following estimation. A good amount of CO_2 would be required to be injected to recover more oil. This method is based on cumulative production of reservoir and rate of CO_2 utilization, which will give us the amount of CO_2 required to recover a barrel of oil.

For this we apply rate at which CO_2 is utilized along with CO_2 recycle rate. First in this method, original oil in place (OOIP) is the ratio of cumulative production to the primary + secondary recovery given by (Equation 4) below. And the reservoirs are assumed to be

near ultimate primary + secondary recovery. For basin average primary + secondary recovery factor will be applied. For an oil reservoir having strong water drive, 50% primary + secondary recovery factor is assumed.(Holtz, López, & Breton, 2005)

$$\mathrm{OOIP} = \frac{\mathrm{N_p}}{\mathrm{R_{ps}}} \quad (4)$$

Where

$\mathrm{OOIP} = \mathrm{Original\ Oil\ in\ place}$

The target recovery estimated by the CO_2 EOR is taken as recovery factor $\mathrm{R_{CO_2}}$, and Ultimate recovery is taken as percentage of OOIP to this recovery by following equation 5.

$$\mathrm{N_{CO_2}} = \mathrm{OOIP} * \mathrm{R_{CO_2}} \quad (5)$$

The net CO_2 required for EOR project is going to be applied through rates of CO_2 utilization. Volume/Amount of CO_2 required is found out as a function of target EOR volume and net rate of utilization (Equation 6). For high permeability sandstone reservoirs, the gross rate of utilization is taken as 4.5 MSCF/STB and the rate of CO_2 recycling as 2 MSCF/STB.

$$\text{Net } \mathrm{CO_2EOR} = \mathrm{N_{CO_2}}(\mathrm{U_{CO_{2T}}} - \mathrm{U_{CO_{2R}}}) \quad (6)$$

Where

$\mathrm{OOIP} = \mathrm{Original\ Oil\ in\ Place(MSTB)}$

$\mathrm{N_p} = \mathrm{Cumulative\ Oil\ Production(MSTB)}$

R_{ps} = Primary + Secondary Recovery

N_{CO_2} = Cumulative CO_2 EOR Target

R_{CO_2} = Ultimate recovery factor from CO_2EOR(% of OIIP)

$U_{CO_{2T}}$ = Total CO_2 utilization (MSCF/STB)

$U_{CO_{2R}}$ = CO_2 utilization recycled(MSCF/STB)

Net CO_2EOR = Net CO_2 used in EOR project(MMSCF)

2.17 Amount of CO_2

Amount of CO_2 required for recovering "X" pore volumes of oil will be calculated by

OOIP= [A.h.Φ.(1- Sw)] / Bo = X bbl of oil (7)

According to the National Petroleum Council (NPC - USA) the net CO_2 utilization factor is about 7.8 Mscf/B of EOR oil.

So as

1 bbl of oil = 7.8 Mscf CO_2 is required

For X barrels of oil

X * 1 bbl of oil = X *7.8 Mscf CO_2 is required

X* 7.8 Mscf of CO_2 is required to replace pore volume of oil present

To convert Scf into ml, we have: $1ft^3$ = 28317 ml

2.18 Permeability as a Measure of Pore-Throat Size:

Permeability has the dimensions of length squared, and various authors have shown that permeability is proportional to the square of pore-throat size times a porosity factor (Nelson and Batzle, 2006). A relation derived by Katz and Thompson (1986) can be written as

$$k \approx 4.48\, d^2 \emptyset^{\,2} \qquad (8)$$

Where K is permeability in md, d is pore size in µm, corresponding to the pressure at which mercury first forms a continuous connected pathway through the sample as measured by the inflection point on a capillary pressure curve and Ø is porosity (Nelson, 2009).

The importance of equation (8) in this work is to select the correct size of the encapsulation for the experiment. In this work encapsulated citric acid is going to be used and as described the size of the encapsulation used must be lower than the pore throat size. Nano-encapsulation is used in this regard. Nano-encapsulation made till date has 200 nm diameter of capsule which is suitable for reservoir application. Acid can be encapsulated to achieve the maximum placement in the reservoir where degradation of capsule is controlled by shell thickness. In this work pore throat size in the encapsulated citric acid experiment can be calculated with the data of porosity and permeability, since the porosity is 0.15 and permeability used is 10.8 md, pore throat size was calculated as 10.35 µm, which is larger than 200 nm size encapsulated citric acid selected for the experiment. So we can use this encapsulated citric acid for encapsulated citric acid experiment.

2.19 Interfacial Tension

Introduction to IFT

Capillary number, a dimensionless number is used as the deterministic parameter to determine the success of any EOR process. D. O. Shah, (1981)

$$N_C = \frac{\mu * v}{\sigma * \cos(\theta)} \quad (9)$$

μ is the viscosity of the displacing fluid

V is the velocity of fluid front

σ is the interfacial tension between wetting and non − wetting fluids

θ is the contact angle between rock and interface of wetting and non − wetting fluid

IFT is measurement of tension between the oil and injected/formation water. IFT is an important parameter determining the microscopic displacement efficiency. Surfactants are usually used to lower the IFT. The carboxylic Group salts like RCOONa,$(RCOO)_2Ca$ will produce higher charge density at the surface of Oil interface with water and will reduce the IFT (E.C. Donaldsonmet et al).

2.20 Effect of Salt Concentration on IFT

It has been shown that salt concentration has important effect to IFT (Foster, 1973; Hill et al. 1973; Chan and Shah, 1977b). IFT decreases with increase in salt concentration, up to a certain (critical) value of salt concentration at which it becomes minimal. And after that it again starts to increase. Lower interfacial tension between the oil and a salt containing

petroleum sulfonate will occur at a lower surfactant concentration for a paraffinic crude and higher NaCl concentration for a naphthenic crude.

Crude oils with high aromatic hydrogen content produce low IFT compared to crude with lower hydrogen content. Gale and Sandvik, (1973)

2.21 Effect of Interfacial charge on IFT

It has been studied that interfacial charge influences IFT significantly. For several systems minimum of IFT and maximum of electrophoretic mobility which is an indirect measure of interfacial charge density, has a definite correlation with IFT for oil surfactant systems. The graph below shows electrophoretic mobility and interfacial tension is taken as the function of concentration surfactant for TRS 10-80-n-octane-brine system. System exhibits minimum IFT at 0.05% TRS 10-80 concentration and electrophoretic mobility has the maximum at the same. It can be seen that electrophoretic mobility and IFT are mirror image to each other.

For a particular concentration of NaOH, IFT between crude oil and caustic solution exhibits a minimum. In order to understand electrophoretic measurements are needed to understand this behavior. The measurements are shown below and, it is understood that at the minimum IFT value electrophoretic mobility is maximum, which can be identified as maximum charge density at oil- caustic interface.

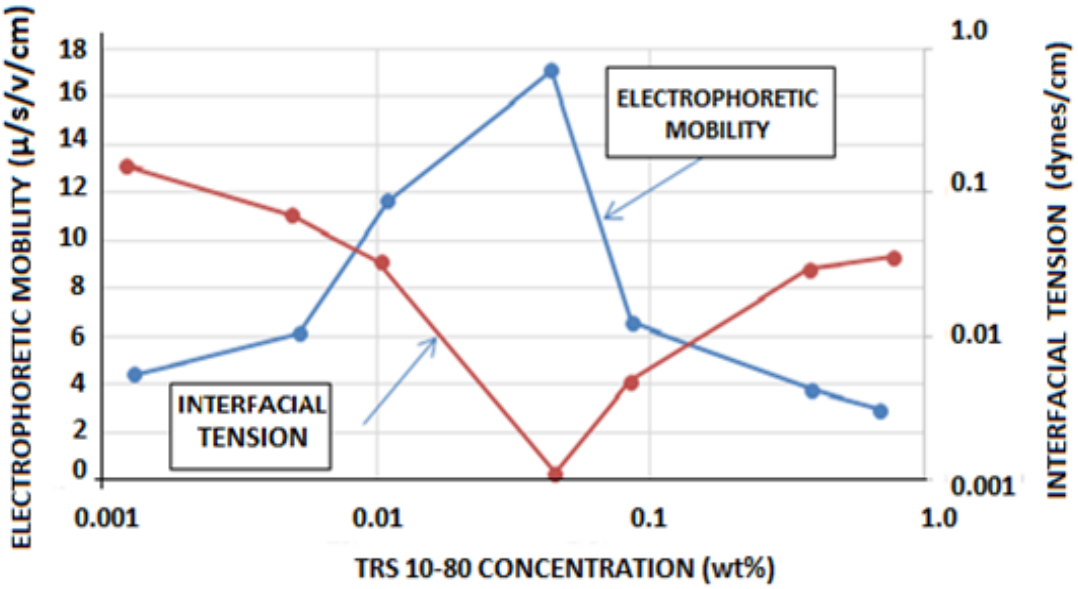


Figure 2-21: TRS 10-80 IN 1% NaCl with n-OCTANE, T= 28°C (Chan and Shah 1980)

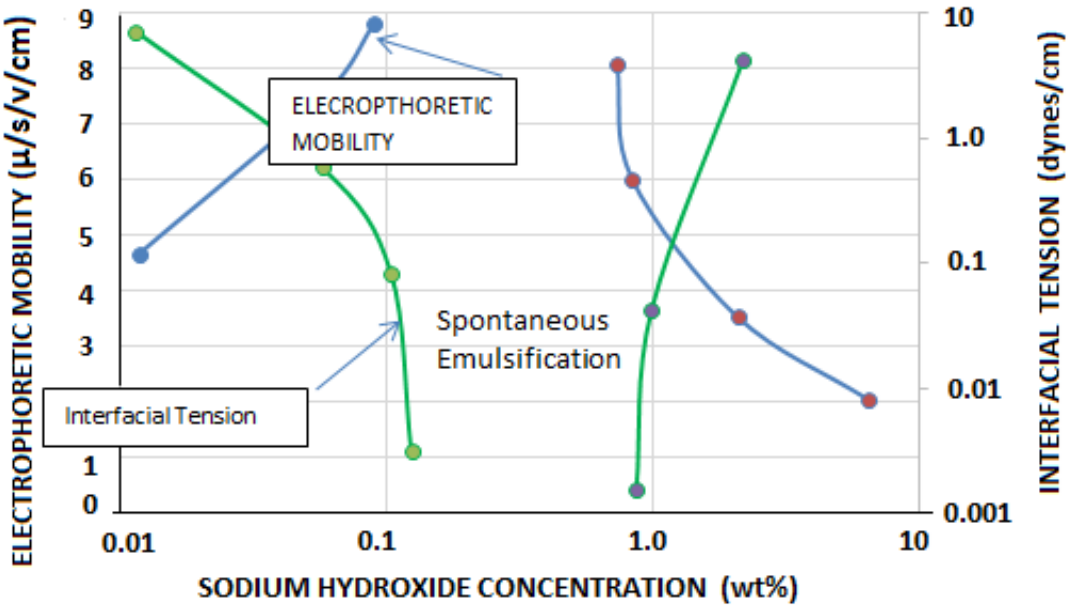


Figure 2-22: TRS 10-80 IN 1% NaCl with n-OCTANE, T= 28°C (Bansal and Shah, 1978)

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Acid Preparation

Acid will be prepared at different concentrations of 2wt%, 5wt%, 7.5wt% and 10wt%. The amount of acid in solid powder form will be used to prepare required acidic solution. The calculation needed for this acid preparation is as follows.

To prepare a 2wt% percent solution following calculations are needed to be done

For 2 wt% percent citric acid solution, total no of grams of citric acid needed = $\frac{2}{100} * 1000 = 20 gram$

20 gram citric acid is needed to prepare 1M solution of 2 wt %, but as we have citric acid powder in mono hydrated form i.e. $C_6H_8O_7.H_2O$ = $\frac{192}{210} = 91.429\%$, we have pure citric acid as 91.429%. So exact amount in grams of this mono hydrated powder used would be= $\frac{20*100}{91.429} = 21.875\ gram$

So for preparing 1000ml of 2wt% citric acid solution 21.875 gram of mono hydrated powder was used. Similarly for 5wt%, 7.5wt% and 10wt% 54.6875 gram, 82.03125 gram, 109.375 gram was used respectively.

This acid will be prepared in sea water solution; the concentration of brine is shown in table 3-1.

3.2 Core Flooding Procedure

3.2.1 Brine Preparation

The concentrations of brines according to the Saudi reservoir connate water and sea-water are as follows. The brines shall be stirred and heated for 24 hours prior to usage in the experiment.

The concentrations are as under:

Table 3-1: Brine concentration

Ions	Connate Water	Sea Water
Sodium	59,491	18,300
Calcium	19,040	650
Magnesium	2,439	2,110
Sulfate	350	4,290
Bicarbonate	354	120
TDS	213,734	57,670

3.2.2 Citric Acid Solution Preparation

Citric Acid solution was prepared using mono hydrated citric acid powder. As described in section 3.1.

3.2.3 Measurement of Core Properties

Core dimensions are measured, i.e. dry weight, length, diameter, and bulk volume. These measurements are required for the porosity calculations. Once the core is saturated with the formation brine, then the wet weight will be measured to get the porosity and the pore volume.

3.2.4 Core Saturation

Core saturation was performed in a cylinder under 1000 psi pressure.

3.2.5 Core Loading

Core was then loaded in to the oven after pressure testing of the core holder.

3.2.6 Formation Brine Saturation

Cores are re-saturated with formation brine and a pressure up to reservoir pressure is built. Overburden pressure was kept 1500 psi was provided from the pump associated with the core flooding system. 500 psi back pressure was applied with nitrogen gas cylinder.

3.2.7 Oil Saturation

Oil used for all experiments is Uthmania oil with 30^{O}API.

3.2.8 Heating of the system

The oven is then started to heat the system gradually to 100°C. Cores are then left for aging.

3.2.9 Water Flooding

Water flooding is done with 0.5cc/min and until all the possible recoverable oil is displaced from the cores i.e. residual oil saturation is achieved.

3.2.10 Citric Acid Injection

Citric acid was then injected with varying concentrations (2wt%, 5wt%, 7.5wt%, and 10wt %) in different sets of experiments. The injection rate of 0.25cc/min and 0.5cc/min was used in the experiments.

3.2.11 Water Flooding

After the citric acid injection again water flood the cores with injection rate of 0.5cc/min and recover the maximum oil.

The oven was then switched off after the experiment was done, after each experiment run system was cleaned to prepare for next experiment.

3.2.12 Permeability Measurement from Core Flooding

Permeability of the core can be measured from core flooding. After Cores are loaded to the system and pressure tested. Cores are then flooded with brine solution starting from the low rate of 0.25 and followed by 0.5, 0.75 and 1 cc, delta p is measured for each flow rate and then by plotting Flow rate Q vs Δp, as shown in graph below, we get a straight line, and its slope is used to calculate permeability with the following relation from Darcy law

$$\frac{Q}{\Delta p} = m = \frac{k\,A}{\mu L} \qquad (10)$$

Where

Q is the flow rate, ml/s

Δp is the change is pressure, atm

k is permeability is darcy

A is the cross-sectional area of the formation, cm^2

μ is the viscosity of the fluid,centipoise

L is the length of the porous media the fluid will flow through, cm

$$k = \frac{m\,\mu L}{A} \tag{11}$$

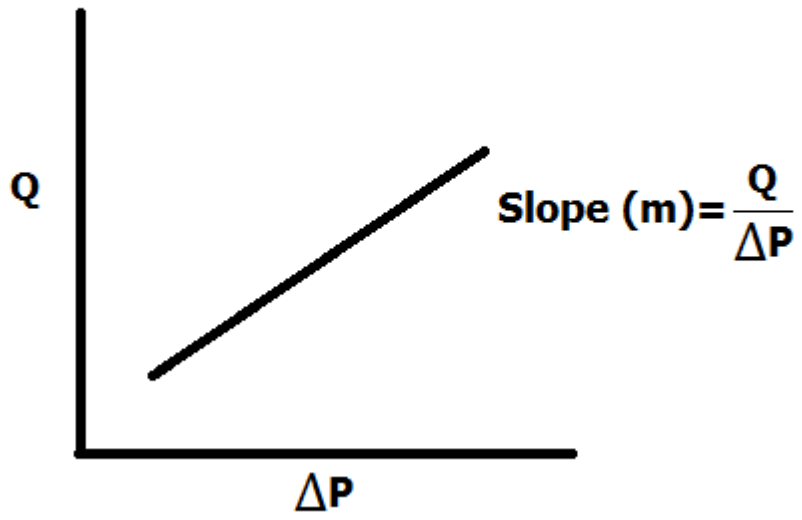


Figure 3-1: Permeability Determination From Core Flood Experiment

3.2.13 Pore Volume Calculation

Pore volume is calculated by first measuring the dry weigh of the core, and then core is saturated with formation brine at a pressure of 1000psi, and wet weight is measured using weigh balance. Pore volume is given by

$$\text{Pore Volume} = \frac{(\text{wet weight} - \text{Dry weight})}{\text{Density of Formation Brine}} \quad (12)$$

Where

Weight is in g

Density in g/cc

3.3 Core Flooding Experiments

All the experiments will be performed using FDES-645Z (by CORETEST SYSTEM, INC). Fig. 3-2 shows the outside front of the system and main required components description. Fig. 3-3 shows inside oven components. The detailed use of system is present in the step by step procedure.

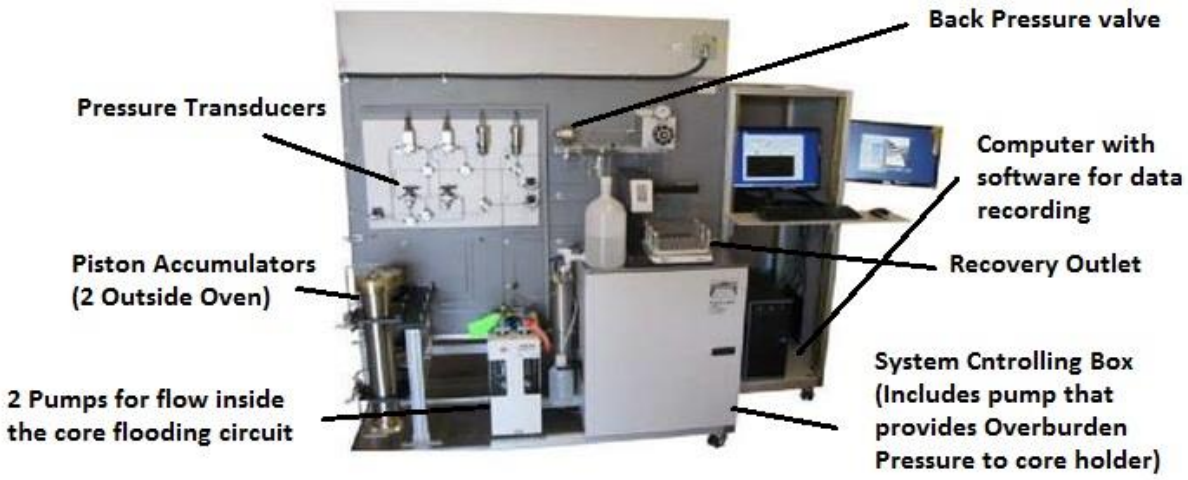


Figure 3-2 : Core flooding system front panel Outside Oven

Figure 3-3 : Core flooding system Inside Oven Horizontal Flow Setup

3.3.1 Experiment #1 (Citric acid 2wt %)

For the first test core with dimensions of 30.45cm in length and 3.8cm in diameter was loaded in to the system. And pore volume was calculated

$$\text{Pore Volume} = \frac{(\text{weight of saturated core} - \text{Dry core})}{Density\ of\ satirating\ liquid}$$

$$\text{Pore Volume} = \frac{(821.911-756.616)}{1.13196}$$

$$\text{Pore Volume} = 57.683$$

Bulk Volume = $\pi r^2 l$=171.7313

$$\text{Porosity} = \frac{Pore\ Volume}{Bulk\ Volume}$$

$$\text{Porosity} = \frac{57.683}{171.7313} = 0.167$$

Details of the Experiment 1 properties are as follows

Pore volume= 57.7 ml

Porosity = 0.167

Permeability = 70.8md

Sw_i = 30.22%

OOIP= 40.25ml

Flow rate = 0.5 cc/min

Back Pressure = 500 psi

Confining/Overburden Pressure = 1500 psi

Core flooding was performed in FDES-645Z (by CORETEST SYSTEM, INC).

Following is the step by step procedure of the test

1) The core was loaded to the system inside a core holder provided with the system, which has two connections as inlet and outlet for applying confining pressure and the third one for the pressure and temperature sensor, the core holder is made of hest-alloy, which is anti-corrosive material.
2) The core is inserted to the rubber sleeve first that has one side connected to a threaded (fixed) connector while the other does not have any thread (movable, to account for the expansion due to the heat applied to the system during core-flooding).
3) After the core has been inserted in the rubber sleeve, inlet and outlet tubing's is connected which have three lines.
4) This core holder was then connected with the core flood system (only three lines of confining inlet, outlet and temperature pressure sensor is connected) and confining pressure (around 1000psi) was applied through the booster pump and the system was left for 6 hours, to check for the leaks, if pressure does not fall below 800 psi it means there is no leak and we can carry forward experiment.
5) Now all the circuit lines flowing to the inlet and outlet of the core holder were connected, Now Start the pump with the rate of 2cc/minute and flow is taken from cylinder 2 having formation water(valves of this cylinders are open i.e. valve no 18)then confining pressure up to 1500psi and then start applying BPR(back pressure) through back pressure valve, initially apply hundred and when BPR inside

the core becomes stable around 100 increase it to 200 and following same way increase it till 500psi.

6) Start data logging and record data.
7) Now start flowing with the rate of 1 cc/min and starting recording dp current by taking the pressure transducer in line, when the dp current gets stabilized , shift to 0.75 cc/min and following same procedure with 0.5 and 0.25cc/min
8) Data logging off now.
9) Plot the dp/q, and get the slope of the line and using Darcy law find permeability.
10) Now start data logging for oil flow.
11) After permeability is known, Start flowing oil from cylinder 4, and opening valve no 16, at the rate of 0.5cc/min, and shift the flow to a measuring cylinder to record the flow and flow until you reach near the value of connate water saturation.
12) After that start applying heat and reach value of 100^{o}C in steps, Confining pressure is increased which is released by the BPR regulator and Pump Air valves, (for small change BPR regulator works like 100 psi but if confining is continuously increasing then Pump air regulator should be used to reduce confining pressure)
13) When the temperature reached 100^{o}C, and flow of 0.5cc/min was maintained with BPR of 500 psi and confining of 1500psi, after that switched the flow to 0.1 cc/min, and left for aging with the continuous flow of oil as well to recover as much as formation water to exactly account for connate water saturation
14) Leave the system for aging for 40 hours (System flow was monitored every 2 hours to insure the flow is maintained and no pressure increase or decrease occurred.

15) After 40 hours of aging, flow was restarted at 0.5cc/min for 2 Pore Volume, then recovery mechanism was adopted
16) First 5 pore volume of sea water was injected with the rate of 0.5cc/min and recovery was recorded with graduated tubes
17) Then 3 pore volume of Citric acid 2wt% was injected with the rate of 0.5cc/min and recovery was recorded with graduated tubes
18) At last, again started flowing sea water with the rate of 0.5 cc/min and continued until no more oil was recovered, a total of 4 Pore volume was injected

3.3.2 Experiment #2 (Citric acid 10wt %)

For the first test core with dimensions of 15.15cm in length and 3.8cm in diameter was loaded in to the system. And pore volume was calculated

$$\text{Pore Volume} = \frac{(409.297-376.299)}{1.13196}$$

$$\text{Pore Volume} = 29.15\text{ml}$$

Bulk Volume = $\pi r^2 l$=171.7313

Porosity = $\frac{29.15}{171.7313}$ = 0.17

Details of the Experiment 2 properties are as follows

Porosity = 0.17

Permeability= 69.8 md

Sw_i = 27.95%

OOIP= 21 ml

Flow rate = 0.5 cc/min

Back Pressure = 500 psi

Confining/Overburden Pressure = 1500 psi

Core flooding was performed in FDES-645Z (by CORETEST SYSTEM, INC). Following is the step by step procedure of the test

1) The core was loaded to the system inside a core holder provided with the system, which has two connections as inlet and outlet for applying confining pressure and the third one for the pressure and temperature sensor, the core holder is made of hest-alloy, which is anti-corrosive material.
2) The core is inserted to the rubber sleeve first that has one side connected to a threaded (fixed) connector while the other does not have any thread (movable, to account for the expansion due to the heat applied to the system during core-flooding).
3) After the core has been inserted in the rubber sleeve, inlet and outlet tubing's were connected which have three lines.
4) This core holder was then connected with the core flood system (only three lines of confining inlet, outlet and temperature pressure sensor is connected) and confining pressure (around 1000psi) was applied through the booster pump and the system was left for 6 hours, to check for the leaks, if pressure does not fall below 800 psi it means there is no leak and we can carry forward experiment.

5) Now all the circuit lines flowing to the inlet and outlet of the core holder were connected, Started the pump with the rate of 2cc/minute and flow was taken from cylinder 2 having formation water(valves of this cylinders are open i.e. valve no 18)then confining pressure up to 1500psi and then start applying BPR(back pressure) through back pressure valve, initially apply 100 psi and when BPR inside the core becomes stable around 100 increase it to 200 and following same way increase it till 500psi.
6) Start data logging and record data.
7) Now start flowing with the rate of 1 cc/min and starting recording dp current by taking the pressure transducer in line, when the dp current gets stabilized , shift to 0.75 cc/min and following same procedure with 0.5 and 0.25cc/min, dp current was recorded.
8) Data logging off now.
9) Plot the dp/q, and get the slope of the line and using Darcy law find permeability.
10) Now start data logging for oil flow.
11) After permeability is known, Start flowing oil from cylinder 4, and opening valve no 16, at the rate of 0.5cc/min, and shift the flow to a measuring cylinder to record the flow and flow until you reach near the value of connate water saturation.
12) after that start applying heat and reach value of 100^{o}C in steps, Confining pressure is increased which is released by the BPR regulator and Pump Air valves, (for small change BPR regulator works like 100 psi but if confining is continuously increasing then Pump air regulator should be used to reduce confining pressure)

13) When the temperature reached 100°C, and flow of 0.5cc/min was maintained with BPR of 500 psi and confining of 1500psi, after that switched the flow to 0.1 cc/min, and left for aging with the continuous flow of oil as well to recover as much as formation water to exactly account for connate water saturation
14) Leave the system for aging for 40 hours (System flow was monitored every 2 hours to insure the flow is maintained and no pressure increase or decrease occurred.
15) After 40 hours of aging, flow was restarted at 0.5cc/min for 2 Pore Volume, then recovery mechanism was adopted
16) First 5 pore volume of sea water was injected with the rate of 0.5cc/min and recovery was recorded with graduated tubes
17) Then 3 pore volume of Citric acid was injected with the rate of 0.5cc/min and recovery was recorded with graduated tubes
18) At last, again started flowing sea water with the rate of 0.5 cc/min and continued until no more oil was recovered, a total of 5 Pore volume was injected

3.3.3 Experiment #3 (Citric acid 5wt %)

For the first test core with dimensions of 15.20cm in length and 3.8cm in diameter was loaded in to the system. And pore volume was calculated

$$\text{Pore Volume} = \frac{(410.648-377.541)}{1.13196}$$

$$\text{Pore Volume} = 29.248\text{ml}$$

$$\text{Porosity} = \frac{29.248}{172.29} = 0.17$$

Details of the Experiment 3 properties are as follows

Porosity = 0.17

Permeability= 73 md

Sw_i =26%

OOIP= 21.65ml

Flow rate = 0.5 cc/min

Back Pressure = 500 psi

Confining/Overburden Pressure = 1500 psi

Core flooding was performed in FDES-645Z (by CORETEST SYSTEM, INC). Following is the step by step procedure of the test

1) The core was loaded to the system inside a core holder provided with the system, which has two connections as inlet and outlet for applying confining pressure and the third one for the pressure and temperature sensor, the core holder is made of hest-alloy, which is anti-corrosive material.
2) The core is inserted to the rubber sleeve first that has one side connected to a threaded (fixed) connector while the other does not have any thread (movable, to account for the expansion due to the heat applied to the system during core-flooding).
3) After the core has been inserted in the rubber sleeve, inlet and outlet tubing's were connected which have three lines.

4) This core holder was then connected with the core flood system (only three lines of confining inlet, outlet and temperature pressure sensor is connected) and confining pressure (around 1000psi) was applied through the booster pump and the system was left for 6 hours, to check for the leaks, if pressure does not fall below 800 psi it means there is no leak and we can carry forward experiment.
5) Now all the circuit lines flowing to the inlet and outlet of the core holder were connected, Started the pump with the rate of 2cc/minute and flow was taken from cylinder 2 having formation water(valves of this cylinders are open i.e. valve no 18)then confining pressure up to 1500psi and then start applying BPR(back pressure) through back pressure valve, initially apply 100 psi and when BPR inside the core becomes stable around 100 increase it to 200 and following same way increase it till 500psi.
6) Start data logging and record data.
7) Now start flowing with the rate of 1 cc/min and starting recording dp current by taking the pressure transducer in line, when the dp current gets stabilized , shift to 0.75 cc/min and following same procedure with 0.5 and 0.25cc/min, dp current was recorded.
8) Data logging off now.
9) Plot the dp/q, and get the slope of the line and using Darcy law find permeability.
10) Now start data logging for oil flow.
11) After permeability is known, Start flowing oil from cylinder 4, and opening valve no 16, at the rate of 0.5cc/min, and shift the flow to a measuring cylinder to record the flow and flow until you reach near the value of connate water saturation.

12) after that start applying heat and reach value of 100°C in steps, Confining pressure is increased which is released by the BPR regulator and Pump Air valves, (for small change BPR regulator works like 100 psi but if confining is continuously increasing then Pump air regulator should be used to reduce confining pressure)
13) When the temperature reached 100°C, and flow of 0.5cc/min was maintained with BPR of 500 psi and confining of 1500psi, after that switched the flow to 0.1 cc/min, and left for aging with the continuous flow of oil as well to recover as much as formation water to exactly account for connate water saturation
14) Leave the system for aging for 40 hours (System flow was monitored every 2 hours to insure the flow is maintained and no pressure increase or decrease occurred).
15) After 40 hours of aging, flow was restarted at 0.5 cc/min for 2 Pore Volume, then recovery mechanism was adopted
16) First 5 pore volume of sea water was injected with the rate of 0.5cc/min and recovery was recorded with graduated tubes
17) Then 3 pore volume of Citric acid 5wt% was injected with the rate of 0.5cc/min and recovery was recorded with graduated tubes
18) At last, again started flowing sea water with the rate of 0.5 cc/min and continued until no more oil was recovered, a total of 1.7 Pore volume was injected

3.3.4 Experiment #4 (Spent Citric acid 10wt %)

For the first test core with dimensions of 15.15 cm in length and 3.8cm in diameter was loaded in to the system. And pore volume was calculated

$$\text{Pore Volume} = \frac{(407.0-368.404)}{1.13196}$$

$$\text{Pore Volume} = 34.097 \text{ ml}$$

$$\text{Porosity} = \frac{34.097}{171.73} = 0.198$$

Details of the Experiment 4 properties are as follows

Porosity = 0.198

Permeability= 73 md

Sw_i =29.31%

OOIP= 24.03 ml

Flow rate = 0.5 cc/min

Back Pressure = 500 psi

Confining/Overburden Pressure = 1500 psi

Core flooding was performed in FDES-645Z (by CORETEST SYSTEM, INC). Following is the step by step procedure of the test

1) The core was loaded to the system inside a core holder provided with the system, which has two connections as inlet and outlet for applying confining pressure and the third one for the pressure and temperature sensor, the core holder is made of hest-alloy, which is anti-corrosive material.
2) The core is inserted to the rubber sleeve first that has one side connected to a threaded (fixed) connector while the other does not have any thread (movable, to

account for the expansion due to the heat applied to the system during core-flooding).

3) After the core has been inserted in the rubber sleeve, inlet and outlet tubing's were connected which have three lines.
4) This core holder was then connected with the core flood system (only three lines of confining inlet, outlet and temperature pressure sensor is connected) and confining pressure (around 1000psi) was applied through the booster pump and the system was left for 6 hours, to check for the leaks, if pressure does not fall below 800 psi it means there is no leak and we can carry forward experiment.
5) Now all the circuit lines flowing to the inlet and outlet of the core holder were connected, Started the pump with the rate of 2cc/minute and flow was taken from cylinder 2 having formation water(valves of this cylinders are open i.e. valve no 18)then confining pressure up to 1500psi and then start applying BPR(back pressure) through back pressure valve, initially apply 100 psi and when BPR inside the core becomes stable around 100 increase it to 200 and following same way increase it till 500psi.
6) Start data logging and record data.
7) Now start flowing with the rate of 1 cc/min and starting recording dp current by taking the pressure transducer in line, when the dp current gets stabilized , shift to 0.75 cc/min and following same procedure with 0.5 and 0.25cc/min, dp current was recorded.
8) Data logging off now.
9) Plot the dp/q, and get the slope of the line and using Darcy law find permeability.

10) Now start data logging for oil flow.
11) After permeability is known, Start flowing oil from cylinder 4, and opening valve no 16, at the rate of 0.5cc/min, and shift the flow to a measuring cylinder to record the flow and flow until you reach near the value of connate water saturation.
12) after that start applying heat and reach value of 100^{o}C in steps, Confining pressure is increased which is released by the BPR regulator and Pump Air valves, (for small change BPR regulator works like 100 psi but if confining is continuously increasing then Pump air regulator should be used to reduce confining pressure)
13) When the temperature reached 100^{o}C, and flow of 0.5cc/min was maintained with BPR of 500 psi and confining of 1500psi, after that switched the flow to 0.1 cc/min, and left for aging with the continuous flow of oil as well to recover as much as formation water to exactly account for connate water saturation
14) Leave the system for aging for 40 hours (System flow was monitored every 2 hours to insure the flow is maintained and no pressure increase or decrease occurred).
15) After 40 hours of aging, flow was restarted at 0.5 cc/min for 2 Pore Volume, then recovery mechanism was adopted
16) First 5 pore volume of spent 10wt% citric acid solution was injected with the rate of 0.5cc/min and recovery was recorded with graduated tubes

3.3.5 Experiment#5 (Citric acid 7.5wt %)

For the first test core with dimensions of 15.0cm in length and 3.8cm in diameter was loaded in to the system. And pore volume was calculated

$$\text{Pore Volume} = \frac{(402.80-368.402)}{1.13196}$$

$$\text{Pore Volume} = 30.415 \text{ ml}$$

$$\text{Porosity} = \frac{30.415}{170.031} = 0.179$$

Details of the Experiment 5 properties are as follows

Porosity = 0.179

Permeability= 71 md

Sw_i = 26%

OOIP= 21.5ml

Flow rate = 0.5 cc/min

Back Pressure = 500 psi

Confining/Overburden Pressure = 1500 psi

Core flooding was performed in FDES-645Z (by CORETEST SYSTEM, INC). Following is the step by step procedure of the test

1) The core was loaded to the system inside a core holder provided with the system, which has two connections as inlet and outlet for applying confining pressure and the third one for the pressure and temperature sensor, the core holder is made of hest-alloy, which is anti-corrosive material.

2) The core is inserted to the rubber sleeve first that has one side connected to a threaded (fixed) connector while the other does not have any thread (movable, to account for the expansion due to the heat applied to the system during core-flooding).
3) After the core has been inserted in the rubber sleeve, inlet and outlet tubing's were connected which have three lines.
4) This core holder was then connected with the core flood system (only three lines of confining inlet, outlet and temperature pressure sensor is connected) and confining pressure (around 1000psi) was applied through the booster pump and the system was left for 6 hours, to check for the leaks, if pressure does not fall below 800 psi it means there is no leak and we can carry forward experiment.
5) Now all the circuit lines flowing to the inlet and outlet of the core holder were connected, Started the pump with the rate of 2cc/minute and flow was taken from cylinder 2 having formation water(valves of this cylinders are open i.e. valve no 18)then confining pressure up to 1500psi and then start applying BPR(back pressure) through back pressure valve, initially apply 100 psi and when BPR inside the core becomes stable around 100 increase it to 200 and following same way increase it till 500psi.
6) Start data logging and record data.
7) Now start flowing with the rate of 1 cc/min and starting recording dp current by taking the pressure transducer in line, when the dp current gets stabilized , shift to 0.75 cc/min and following same procedure with 0.5 and 0.25cc/min, dp current was recorded.

8) Data logging off now.
9) Plot the dp/q, and get the slope of the line and using Darcy law find permeability.
10) Now start data logging for oil flow.
11) After permeability is known, Start flowing oil from cylinder 4, and opening valve no 16, at the rate of 0.5cc/min, and shift the flow to a measuring cylinder to record the flow and flow until you reach near the value of connate water saturation.
12) after that start applying heat and reach value of 100^{o}C in steps, Confining pressure is increased which is released by the BPR regulator and Pump Air valves, (for small change BPR regulator works like 100 psi but if confining is continuously increasing then Pump air regulator should be used to reduce confining pressure)
13) When the temperature reached 100^{o}C, and flow of 0.5cc/min was maintained with BPR of 500 psi and confining of 1500psi, after that switched the flow to 0.1 cc/min, and left for aging with the continuous flow of oil as well to recover as much as formation water to exactly account for connate water saturation
14) Leave the system for aging for 40 hours (System flow was monitored every 2 hours to insure the flow is maintained and no pressure increase or decrease occurred).
15) After 40 hours of aging, flow was restarted at 0.5 cc/min for 2 Pore Volume, then recovery mechanism was adopted
16) First 5 pore volume of sea water was injected with the rate of 0.5cc/min and recovery was recorded with graduated tubes
17) Then 3 pore volume of Citric acid 7.5wt% was injected with the rate of 0.5cc/min and recovery was recorded with graduated tubes

18) At last, again started flowing sea water with the rate of 0.5 cc/min and continued until no more oil was recovered, a total of 5 Pore volume was injected

3.3.6 Experiment#6 (Encapsulated Citric acid 10wt %)

For the first test core with dimensions of 15.24cm in length and 3.8cm in diameter was loaded in to the system. And pore volume was calculated

$$\text{Pore Volume} = 26.04929\text{ml}$$

$$\text{Porosity} = \frac{26.04929}{172.75} = 0.15$$

Details of the Experiment 6 properties are as follows

Porosity = 0.179

Permeability= 10.8 md

Sw_i = 27%

OOIP= 19.01598 ml

Flow rate = 0.25 cc/min

Back Pressure = 500 psi

Confining/Overburden Pressure = 1500 psi

Core flooding was performed in FDES-645Z (by CORETEST SYSTEM, INC). Following is the step by step procedure of the test

1) The core was loaded to the system inside a core holder provided with the system, which has two connections as inlet and outlet for applying confining pressure and the third one for the pressure and temperature sensor, the core holder is made of hest-alloy, which is anti-corrosive material.
2) The core is inserted to the rubber sleeve first that has one side connected to a threaded (fixed) connector while the other does not have any thread (movable, to account for the expansion due to the heat applied to the system during core-flooding).
3) After the core has been inserted in the rubber sleeve, inlet and outlet tubing's were connected which have three lines.
4) This core holder was then connected with the core flood system (only three lines of confining inlet, outlet and temperature pressure sensor is connected) and confining pressure (around 1000psi) was applied through the booster pump and the system was left for 6 hours, to check for the leaks, if pressure does not fall below 800 psi it means there is no leak and we can carry forward experiment.
5) Now all the circuit lines flowing to the inlet and outlet of the core holder were connected, Started the pump with the rate of 2cc/minute and flow was taken from cylinder 2 having formation water(valves of this cylinders are open i.e. valve no 18)then confining pressure up to 1500psi and then start applying BPR(back pressure) through back pressure valve, initially apply 100 psi and when BPR inside the core becomes stable around 100 increase it to 200 and following same way increase it till 500psi.
6) Start data logging and record data.

7) Now start flowing with the rate of 1 cc/min and starting recording dp current by taking the pressure transducer in line, when the dp current gets stabilized , shift to 0.75 cc/min and following same procedure with 0.5 and 0.25cc/min, dp current was recorded.
8) Data logging off now.
9) Plot the dp/q, and get the slope of the line and using Darcy law find permeability.
10) Now start data logging for oil flow.
11) After permeability is known, Start flowing oil from cylinder 4, and opening valve no 16, at the rate of 0.5cc/min, and shift the flow to a measuring cylinder to record the flow and flow until you reach near the value of connate water saturation.
12) after that start applying heat and reach value of 100^{o}C in steps, Confining pressure is increased which is released by the BPR regulator and Pump Air valves, (for small change BPR regulator works like 100 psi but if confining is continuously increasing then Pump air regulator should be used to reduce confining pressure)
13) When the temperature reached 100^{o}C, and flow of 0.5cc/min was maintained with BPR of 500 psi and confining of 1500psi, after that switched the flow to 0.1 cc/min, and left for aging with the continuous flow of oil as well to recover as much as formation water to exactly account for connate water saturation
14) Leave the system for aging for 40 hours (System flow was monitored every 2 hours to insure the flow is maintained and no pressure increase or decrease occurred.
15) After 40 hours of aging, flow was restarted at 0.25cc/min for 2 Pore Volume, then recovery mechanism was adopted

16) First 2 pore volume of sea water was injected with the rate of 0.25cc/min and recovery was recorded with graduated tubes
17) Then 2 pore volume of Citric acid was injected with the rate of 0.25cc/min and recovery was recorded with graduated tubes, we see no recovery in this scenario because encapsulation shell needs to be broken.
18) So After injection of 2 pore volume of encapsulated citric acid, flow was stopped and 24 hours soaking time was given to make sure encapsulation shell is broken and with the reaction of citric acid and carbonate rock of core CO_2 is generated and mixed with the oil to reduce its viscosity.
19) At last, again started flowing sea water with the rate of 0.25 cc/min and continued until no more oil was recovered, a total of 3 Pore volume was injected

3.4 IFT Measurements

3.4.1 Spent Citric Acid Preparation Calculation

As in this work, we will get calcium citrate as a bi product along with CO_2, so it will have a role in reducing the IFT between the oil and the water. This effect will be measured and confirmed by IFT tests that will be done as discussed below. We need to prepare spent citric acid i.e. all the active acid is used in the reaction and as a result we can study the contribution of oil recovery with the secondary mechanism of IFT reduction. Citric acid reacts with calcium carbonate in following proportions.

$$2C_6H_8O_7 + 3CaCO_3 \longrightarrow Ca_3(C_6H_8O_7)_2 + 3CO_2 \quad (13)$$

Now to calculate how many grams of $CaCO_3$ is needed to react with citric acid, following calculations are needed

$$2C_6H_8O_7 + 3CaCO_3 \longrightarrow Ca_3(C_6H_8O_7)_2 + 3CO_2 \quad (14)$$

For example we take 50ml of 2wt% prepared citric acid solution to react with $CaCO_3$ powder.

50 ml is 20 times of 1000 ml so for each gram of citric acid we need $=\frac{21.875}{20} = 1.09375$ gram

Moles of Citric acid will be= $\frac{mass}{mol\ mass} = \frac{1.09375}{192} = 0.0056966\ moles$

2 moles of citric acid react with = 3 moles of Calcium carbonate

$0.0056966\ moles$ of citric acid react with

$$= \frac{3}{2} * 0.0056966 \text{ moles of Calcium carbonate}$$

Moles of Calcium carbonate $= 0.008545$ moles

Mass of calcium carbonate powder will be = moles * mol mass= $0.008545 * 100$

Mass of calcium carbonate powder will be = 0.8545 gram

3.5 IFT Measurements at High Temperature and Atmospheric Pressure

IFT tests were first carried out in spinning drop apparatus, Interfacial tension was measured for oil versus three solutions i.e. sea water, 2wt% spent citric acid solution prepared with

sea water, 5wt% spent citric acid solution prepared with sea water and 10wt% spent citric acid solution prepared with sea water.

3.5.1 Spent Citric Acid Preparation Procedure

Following are the steps of spent citric acid solution preparation

1. Prepared required 2wt% Citric acid solution in sea water as described in section 3.1.

2. Mixed citric acid with $CaCO_3$ powder and allowed to react for 4 hours with continuous stirring at 50^oC.

3. After the chemical reaction had taken place, the solution was filtered.

4. Following the same steps 5wt%, 7wt% and, 10wt% solution of spent citric acid with sea water were prepared.

5. Measured the IFT of these four solutions sea water, filtrated solution of 2wt% solution of spent citric acid with sea water, filtrated solution of 5wt% solution of spent citric acid with sea water, and filtrated solution of 10wt% solution of spent citric acid with sea water with known oil composition.

3.6 Measurement of Interfacial Tension at HTHP using IFT700

3.6.1 Parts

The basic parts of equipment are viewing cell, injector, bulk pump, drop pump, camera, gauge and the computer software.

3.6.2 Procedure

Two kinds of fluid used in this experiment are:

3.6.3 Bulk Fluid

Refers to the fluid where the droplet is released. Example: Water droplet released in the atmosphere. Air is the bulk fluid.

3.6.4 Drop Fluid:

Refer to nature of the fluid of the droplet. Example: Water droplet released in the atmosphere. Water is the drop fluid.

For Our experiment:

Base Fluid: desired wt% spent citric with $CaCO_3$

Drop fluid: Oil

Cell configuration: Rising drop.

For our experiments we will be running the test at different pressure and temperature conditions and change in IFT will be recorded.

3.6.5 Principle

At room temperature of 30ºC and pressure of 2000 psi, a drop of oil is created from a calibrated capillary (injector) into the bulk fluid inside the viewing cell. For contact angle measurement, a camera connected to a computer records the shape of the drop and the software solves the Laplace equation to provide the interfacial tension and contact angle values.

3.6.6 Steps Experiment No 1: Bulk fluid is Spent Citric Acid 10wt%

The apparatus is cleaned thoroughly with solvent (toluene) and grease remover and sprayed to remove any dirt.

i. Injector is inserted in the bottom position.
ii. Temperature is set to room temperature
iii. 10wt% spent citric with $CaCO_3$ solution was filled in the viewing cell and then filled to the bulk pump.
iv. Pressure gauges show respective pressures. Pressure is increased to 2000 psi by tightening the screw of bulk pump and drop pump. (drop pressure to be kept higher than bulk pressure)
v. Focused camera on to the needle and defined densities of oil and spent citric acid into the software at the condition of 30ºC and 2000 psi.
vi. Performed Calibration of needle manually into the software to identify drop.
vii. Then drop of oil was generated by increasing the oil pressure from the pump.
viii. A bubble is formed, attached to the needle of injector.

ix. When a stable bubble is formed , started IFT measurement in through software and calculated the interfacial tension of oil in 10wt% spent citric with $CaCO_3$ solution at given temperature and pressure by measuring the size of the drop.

x. Image of the drop is saved by the software in the computer.

xi. Repeat Steps 6 to 11 for IFT at 50^oC and 2000 psi.

xii. Repeat Steps 6 to 11 for IFT at 70^oC and 2000 psi.

xiii. Repeat Steps 6 to 11 for IFT at 100^oC and 2000 psi.

xiv. Repeat Steps 6 to 11 for IFT at 100^oC and atmospheric pressure.

xv. Repeat Steps 6 to 11 for IFT at 100^oC and 500 psi.

xvi. Repeat Steps 6 to 11 for IFT at 100^oC and 1000 psi.

xvii. Repeat Steps 6 to 11 for IFT at 100^oC and 1500 psi.

3.6.7 Steps Experiment No 2: Bulk fluid is Spent Citric Acid 5wt%

i. The apparatus is cleaned thoroughly with solvent (toluene) and grease remover and sprayed to remove any dirt.

ii. Injector is inserted in the bottom position.

iii. Temperature is set to room temperature

iv. 5wt% spent citric with $CaCO_3$ solution was filled in the viewing cell and then filled to the bulk pump.

v. Pressure gauges show respective pressures. Pressure is increased to 2000 psi by tightening the screw of bulk pump and drop pump. (drop pressure to be kept higher than bulk pressure)

vi. Focused camera on to the needle and defined densities of oil and spent citric acid into the software at the condition of 30^oC and 2000 psi.

vii. Performed Calibration of needle manually into the software to identify drop.

viii. Then drop of oil was generated by increasing the oil pressure from the pump.

ix. A bubble is formed, attached to the needle of injector.

x. When a stable bubble is formed , started IFT measurement in through software and calculated the interfacial tension of oil in 5wt% spent citric with $CaCO_3$ solution at given temperature and pressure by measuring the size of the drop.

xi. Image of the drop is saved by the software in the computer.

xii. Repeat Steps 6 to 11 for IFT at 50^{o}C and 2000 psi.

xiii. Repeat Steps 6 to 11 for IFT at 70^{o}C and 2000 psi.

xiv. Repeat Steps 6 to 11 for IFT at 100^{o}C and 2000 psi.

xv. Repeat Steps 6 to 11 for IFT at 100^{o}C and atmospheric pressure.

xvi. Repeat Steps 6 to 11 for IFT at 100^{o}C and 500 psi.

xvii. Repeat Steps 6 to 11 for IFT at 100^{o}C and 1000 psi.

xviii. Repeat Steps 6 to 11 for IFT at 100^{o}C and 1500 psi.

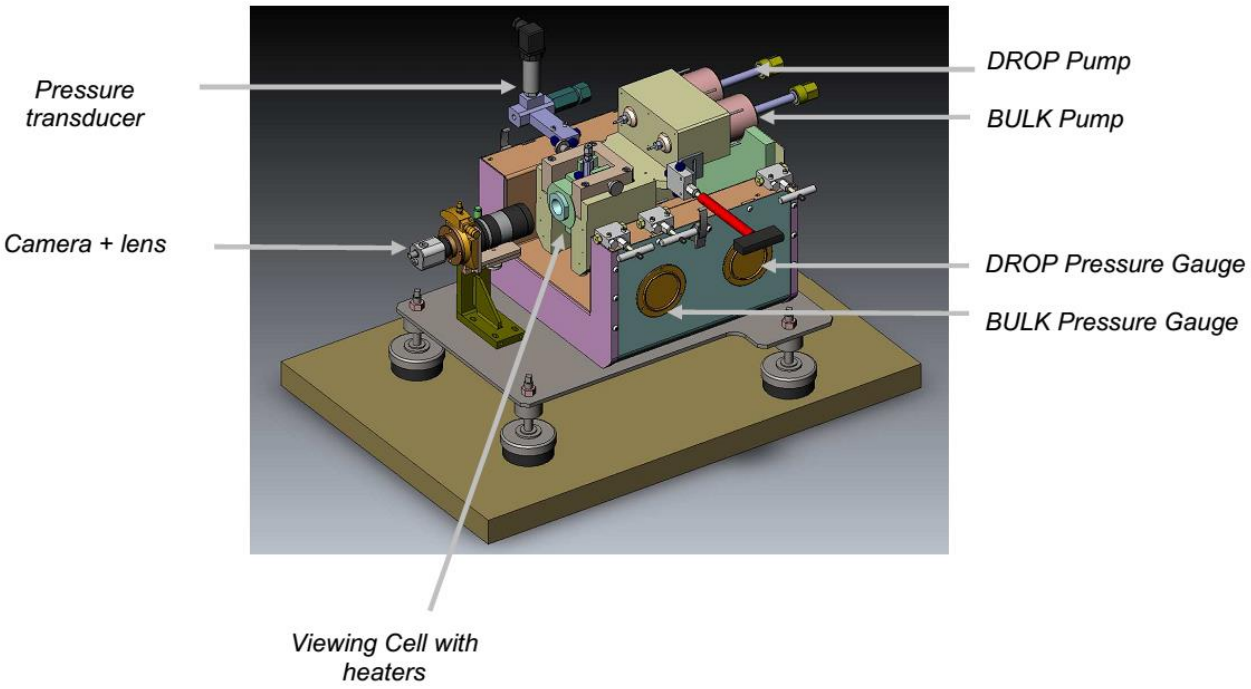


Figure 3-4: Interfacial Tension Equipment IFT700

3.7 CMG Simulations

3.7.1 Reservoir Geometry and Properties

The simulation work is divided in to different case and scenarios. All the simulations are started at with S_{or} condition. The simulation area is at depth of 1000ft from surface and has an area of 8000ft horizontal direction and 6000ft vertical direction. Horizontal was divided in to 50 grid blocks having length of each grid block as 160. Vertical was divided in to 40 grid blocks having length of each grid block as 150. The area is divided into five layers having thickness of 60ft, 80ft, 5ft, 40ft and 30ft respectively. The first three layers are oil zone while the last two layers are aquifer. Porosity and permeability of each layer is divided as 0.18, 0.17, 0.10, 0.18, 0.15 and 100 md, 80 md, 0.01 md 75 md, 90 md respectively. And within the grid block permeability in x, y and z direction is perm x= perm y= 0.1 * perm x. The other properties are Pressure at 1000ft= 4000 psi, MMP= 1600, MINSS= 0.01, P_b = 1400 psi, GOC= 9000 ft.

3.7.2 Well Properties

The defined properties of wells are kept as follows

Maximum injection pressure = 5500 psi, for injectors

Operating BHP = 1800 psi for producers

GOR= 8000 auto well

WCUT= 0.99

STO= 100

Well radius= 0.625

Skin = 1.5

3.7.3 Fluid Properties

Relative permeability data used are as follows. The relative permeability data is considered to be constant after CO_2 flooding. CO_2 will only affect oil viscosity.

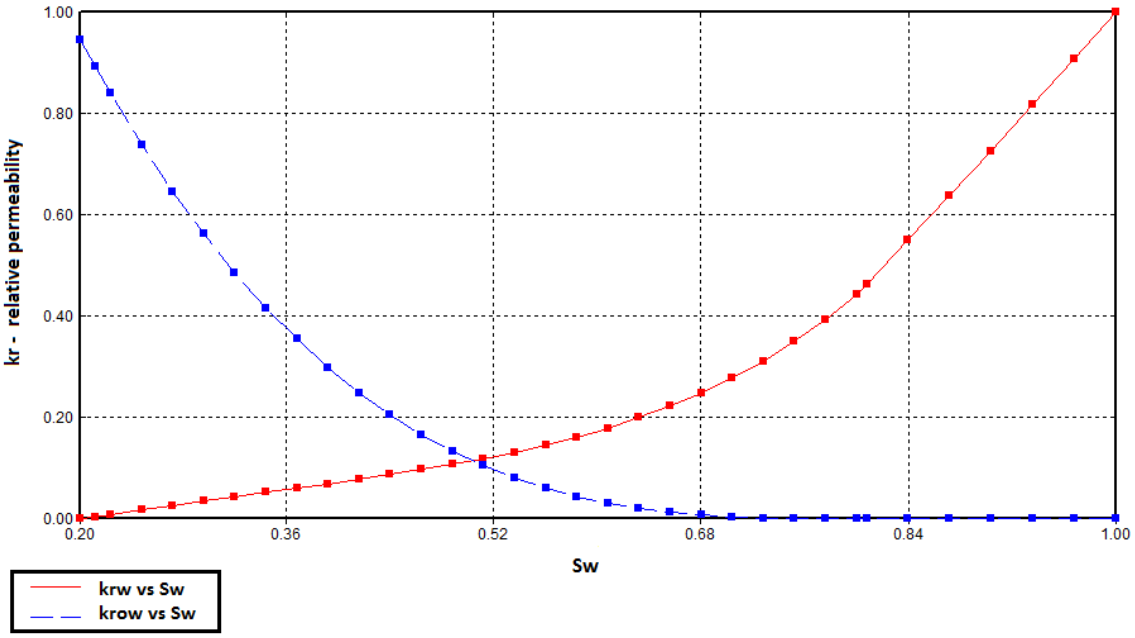


Figure 3-5 : Relative Permeability of water

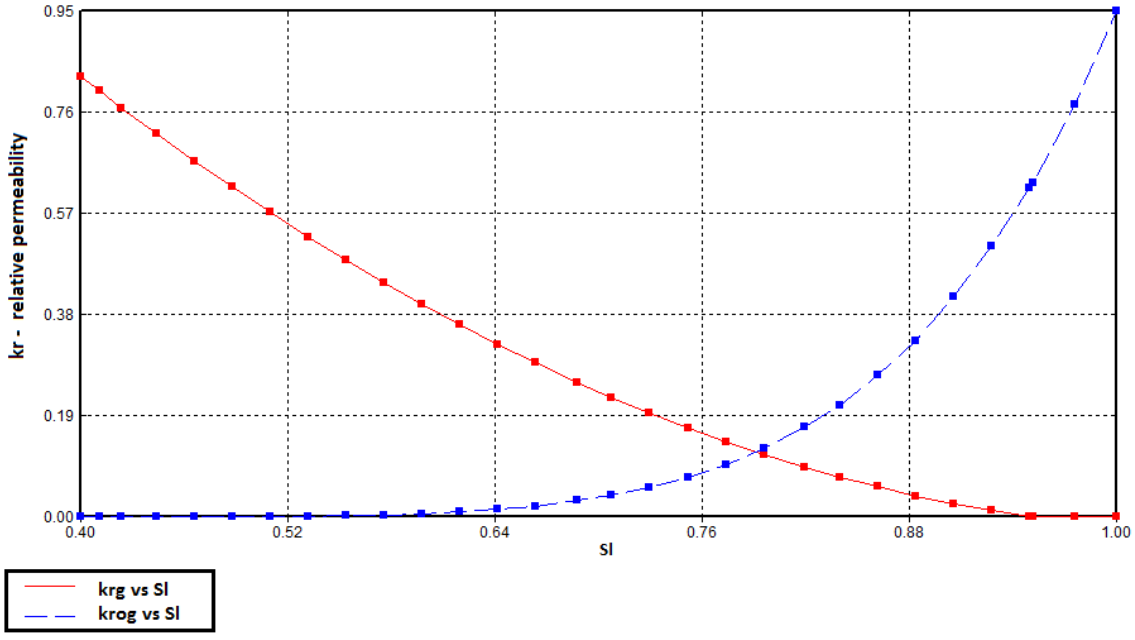


Figure 3-6 : Relative Permeability of Gas

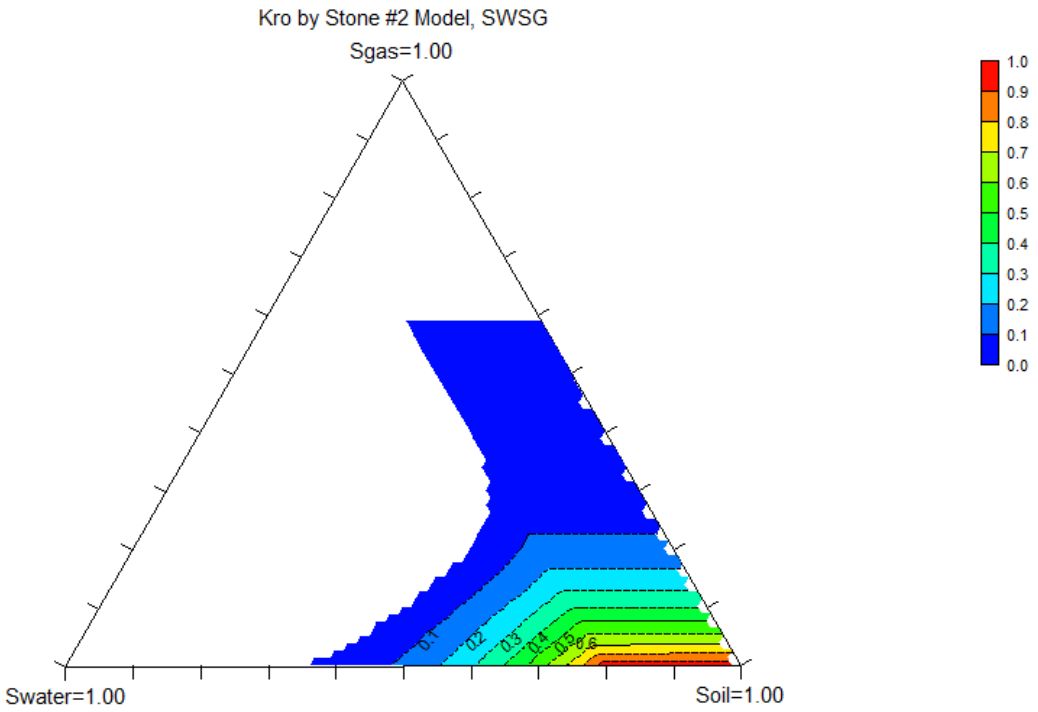


Figure 3-7 : Relative Permeability of Oil

3.8 CMG Simulations with reservoir at S_{or}

There are three different cases in which the simulation is divided in to this particular category

3.8.1 Inject CO_2 in to the reservoir and get recovery from it

Three well schemes are designed in this category

a) Both injector and producer are horizontal(one injector and one producer well)
b) Both injectors and producers are vertical (Three vertical gas injectors and three vertical producers)
c) Vertical injectors and horizontal producers (Three vertical gas injectors and one horizontal producer)

3.8.2 Inject CO_2 in to the aquifer and produce naturally

Three well schemes are designed in this category

a) Both injector and producer are horizontal(one injector and one producer well)
b) Both injectors and producers are vertical (Three vertical gas injectors and three vertical producers)
c) Vertical injectors and horizontal producers (Three vertical gas injectors and one horizontal producer)

3.8.3 Inject CO_2 in to the aquifer followed by water injection and get recovery

Three well schemes are designed in this category

a) Both injector and producer are horizontal(One gas injectors, Two water injectors and one producer well)
b) Both injectors and producers are vertical (Three vertical gas injectors, Three vertical water injectors and Three vertical producers)
c) Vertical injectors and horizontal producers (Three vertical gas injectors, Three vertical water injectors and one horizontal producer)

Further simulations will be ran in this same category that will compare the CO_2 injection versus sea water injection for vertical and horizontal injectors benefit in terms of maximum pressure and corresponding CO_2 saturation that can be achieved for this maximum pressure in each case.

CHAPTER 4

RESULTS & DISCUSSION

4.1 Core Flooding Results

4.1.1 Experiment #1 (Citric acid 2wt %)

Following results were achieved with this test, as shown in Table 4-1 and Fig. 4-1.We injected 5 pore volume of sea water, which recovered 48.3% of OOIP. Initially core is completely saturated with oil and we get maximum amount of oil for the initial 1 pore volume of sea water injection. 5 pore volume of oil was injected to confirm that we cannot recover more from sea water injection. After this we shifted the flow from sea water to 2 wt% citric acid that recovered 5.6% of OOIP. This extra oil is recovered as oil viscosity reduction occurred due to in-situ generation of CO_2 which is generated as a result of citric acid and carbonate rock interaction. After this we again shifted the flow from citric acid to sea water. It can be clearly seen that oil is produced initially with the same increasing trend as before due to citric acid injection, and this is because even if we shift the flow from citric acid to sea water, pores are still filled with part of citric acid that is contributing to increase in oil recovery due to in-situ generation of CO_2. 5 pore volume of sea water was injected to make sure that maximum recoverable oil from sea water injection has been recovered. Sea water injection recovered 6% of OOIP.

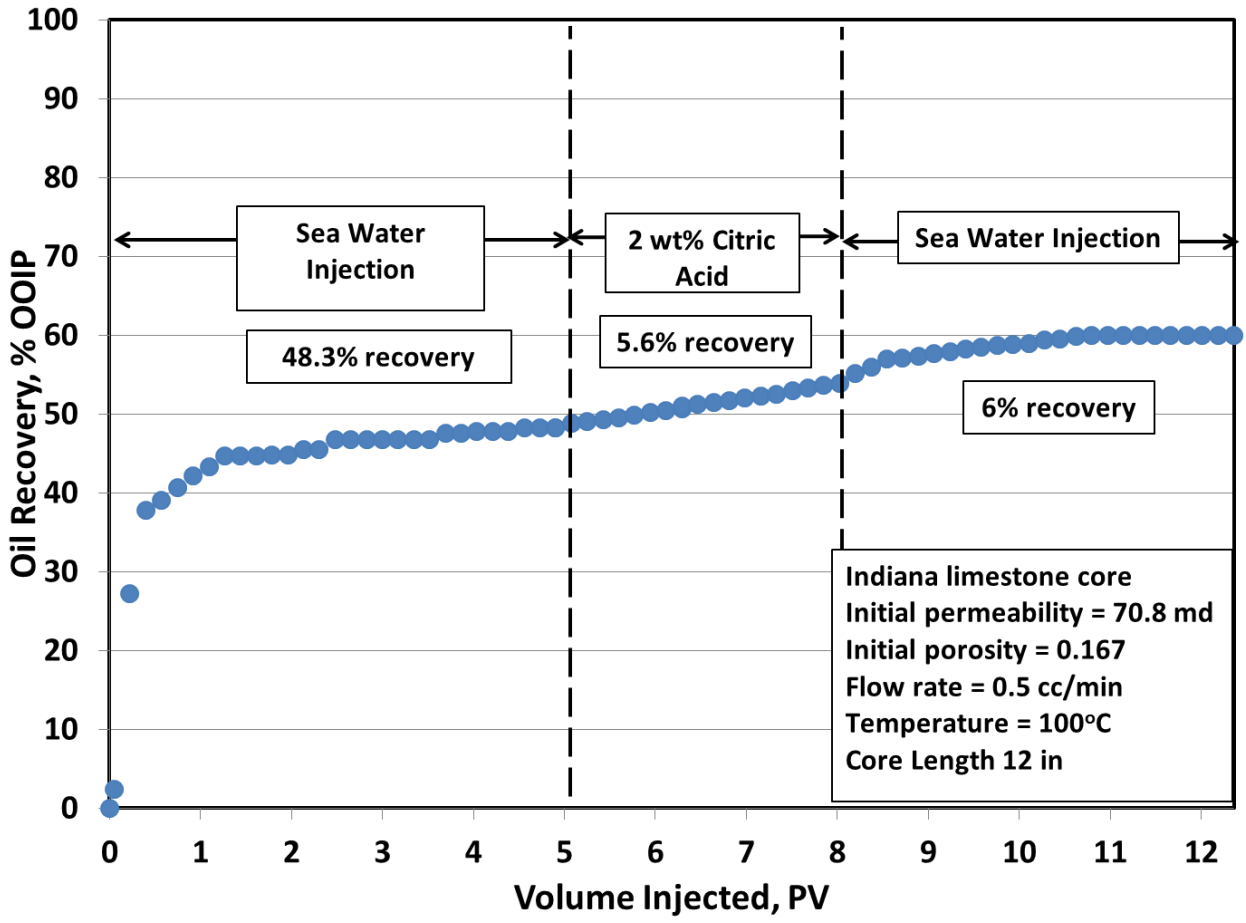
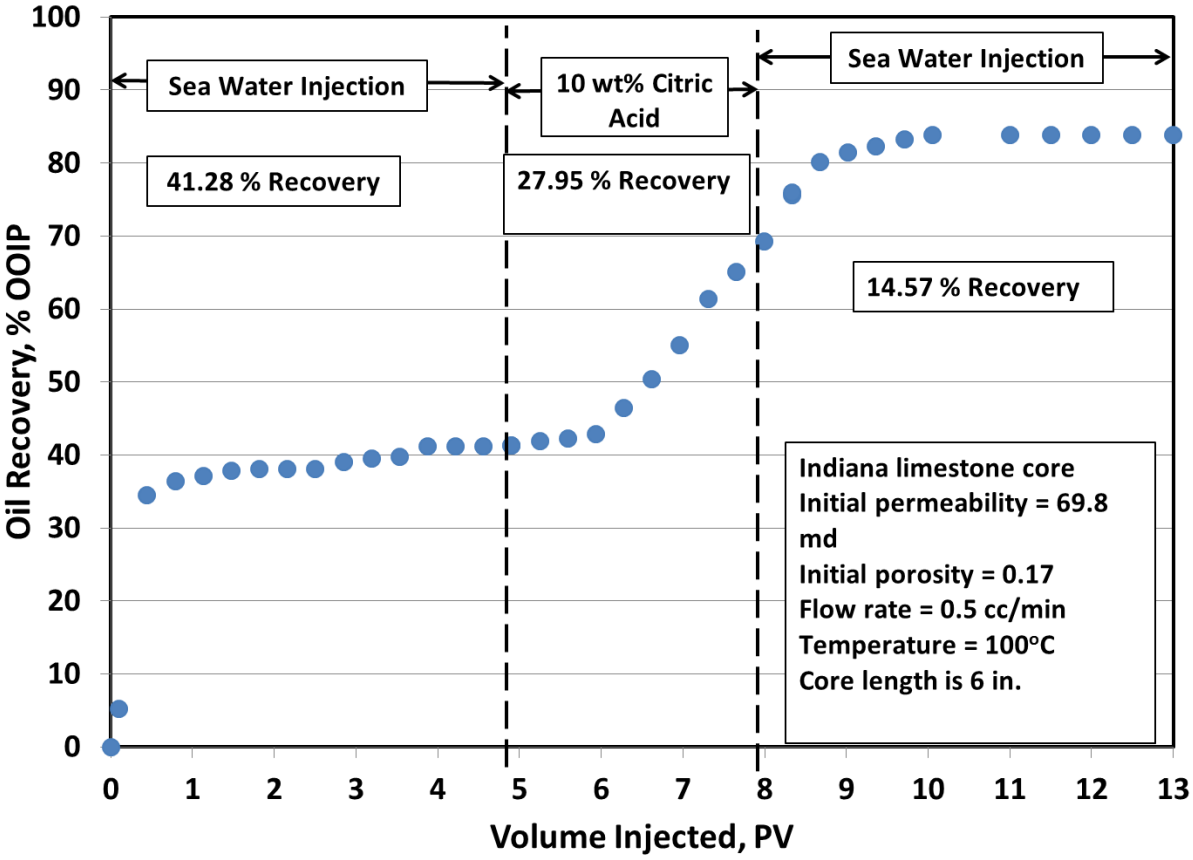


Figure 4-1 : Experiment # 1. Citric Acid 2wt% (Recovery Factor vs PV Injected)

4.1.2 Experiment #2 (Citric acid 10wt %)

Following results were achieved with this test, as shown in Table 4-2 and Fig. 4-2. We injected 5 pore volume of sea water, which recovered 41.28% of OOIP. Initially core is completely saturated with oil and we get maximum amount of oil for the initial 0.5 pore volume of sea water injection. 5 pore volume of oil was injected to confirm that we cannot recover more from sea water injection. After this we shifted the flow from sea water to 10 wt% citric acid that recovered 27.95% of OOIP. This extra oil is recovered as oil viscosity reduction occurred due to in-situ generation of CO_2 which is generated as a result of citric acid and carbonate rock interaction. After this we again shifted the flow from citric acid to sea water. It can be clearly seen that oil is produced initially with the same increasing trend as before due to citric acid injection, and this is because even if we shift the flow from citric acid to sea water pores are still filled with part of citric acid that is contributing to increase in oil recovery due to in-situ generation of CO_2. 5 pore volume of sea water was injected to make sure that maximum recoverable oil from sea water injection has been recovered. Sea water injection recovered 14.57% of OOIP.

Figure 4-2 : Experiment #2. Citric Acid 10wt% (Recovery Factor vs PV Injected)



4.1.3 Experiment #3 (Citric acid 5wt %)

Following results were achieved with this test, as shown in Table 4-3 and Figure 4-3. We injected 5 pore volume of sea water, which recovered 43.4% of OOIP. Initially core is completely saturated with oil and we get maximum amount of oil for the initial 1 pore volume of sea water injection. 5 pore volume of oil was injected to confirm that we cannot recover more from sea water injection. After this we shifted the flow from sea water to 5 wt% citric acid that recovered 3.94% of OOIP. This extra oil is recovered as oil viscosity reduction occurred due to in-situ generation of CO_2 which is generated as a result of citric acid and carbonate rock interaction. After this we again shifted the flow from citric acid to sea water. It can be clearly seen that oil is produced initially with the same increasing trend as before due to citric acid injection, and this is because even if we shift the flow from citric acid to sea water pores are still filled with part of citric acid that is contributing to increase in oil recovery due to in-situ generation of CO_2. 5 pore volume of sea water was injected to make sure that maximum recoverable oil from sea water injection has been recovered. Sea water injection recovered 5.08% of OOIP.

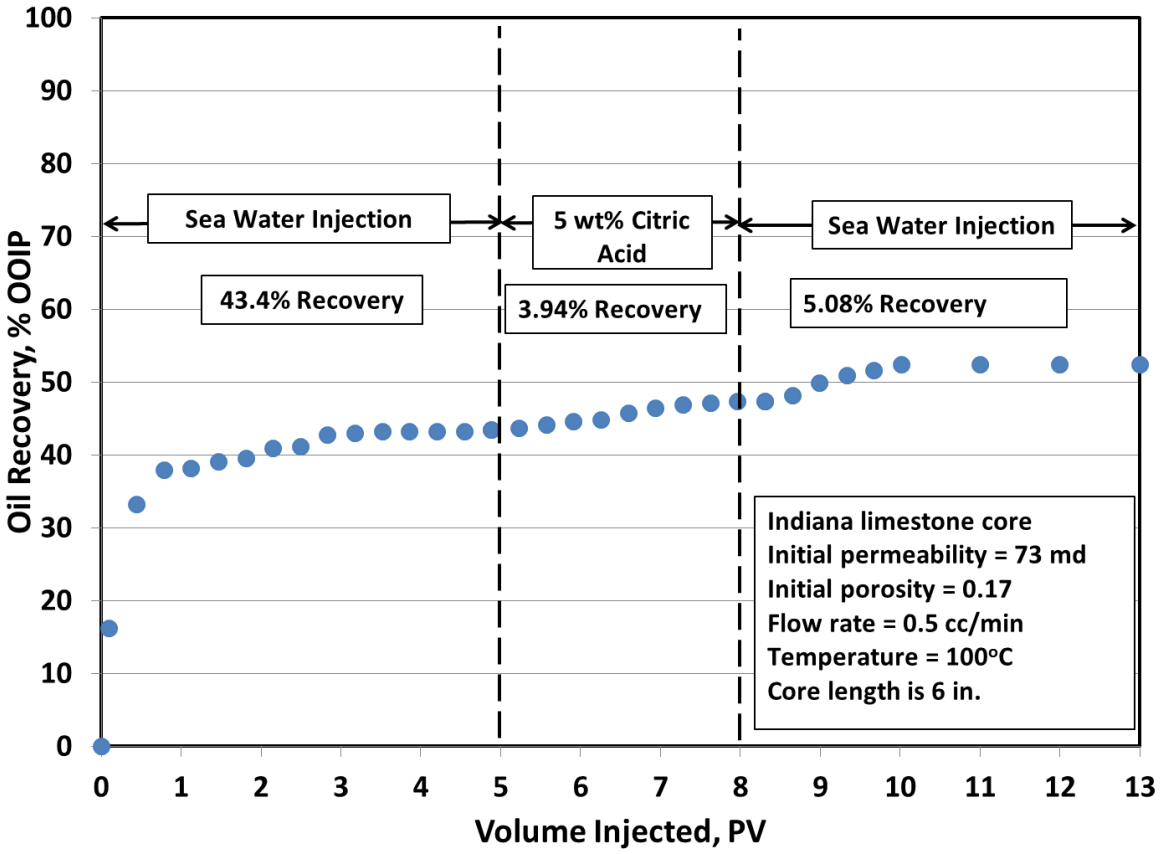


Figure 4-3 : Experiment#3. Citric Acid 7.5wt% (Recovery Factor vs PV Injected)

4.1.4 Experiment #4 (Spent Citric acid 10wt %)

Following results were achieved with this test, as shown in Table 4-4 and Fig. 4-4. In this experiment we injected 5 pore volume of 10 wt% spent citric acid from the start when core is at initial oil saturation. This experiment was conducted to account for the extra oil that can be recovered by the mechanism of IFT reduction. The results show that we were able to achieve extra 8.03% recovery compared to sea water injection, which confirmed that IFT reduction is contributing to additional oil recovery.

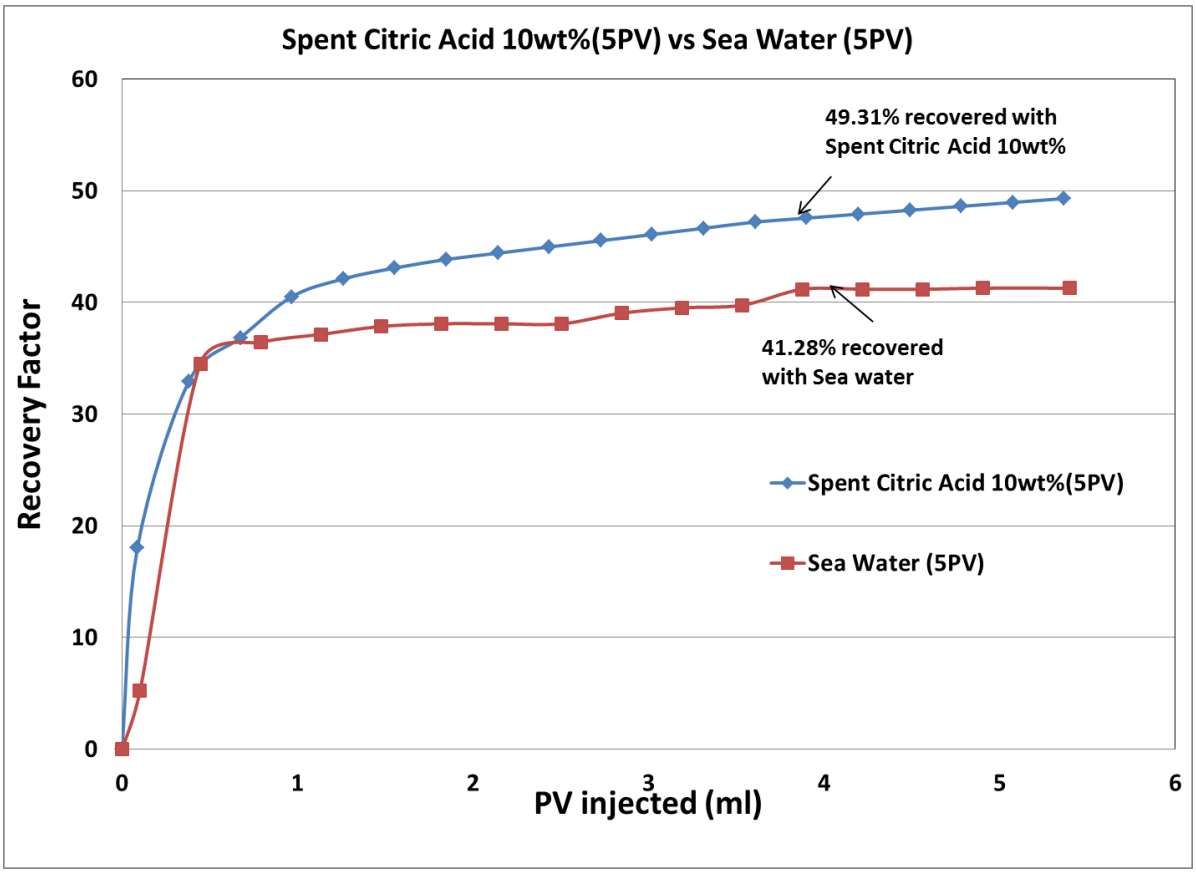


Figure 4-4 : Experiment#4. Spent Citric Acid 10wt %(5PV) vs Sea Water (5PV)

(Recovery Factor vs PV Injected)

4.1.5 Experiment#5 (Citric acid 7.5wt %)

Following results were achieved with this test, as shown in Table 4-5 and Figure 4-5. We injected 5 pore volume of sea water, which recovered 42.55% of OOIP. Initially core is completely saturated with oil and we get maximum amount of oil for the initial 1 pore volume of sea water injection. 5 pore volume of oil was injected to confirm that we cannot recover more from sea water injection. After this we shifted the flow from sea water to 5 wt% citric acid that recovered 23.55% of OOIP. This extra oil is recovered as oil viscosity reduction occurred due to in-situ generation of CO_2 which is generated as a result of citric acid and carbonate rock interaction. After this we again shifted the flow from citric acid to sea water. It can be clearly seen that oil is produced initially with the same increasing trend as before due to citric acid injection, and this is because even if we shift the flow from citric acid to sea water pores are still filled with part of citric acid that is contributing to increase in oil recovery due to in-situ generation of CO_2. 5 pore volume of sea water was injected to make sure that maximum recoverable oil from sea water injection has been recovered. Sea water injection recovered 7.95% of OOIP.

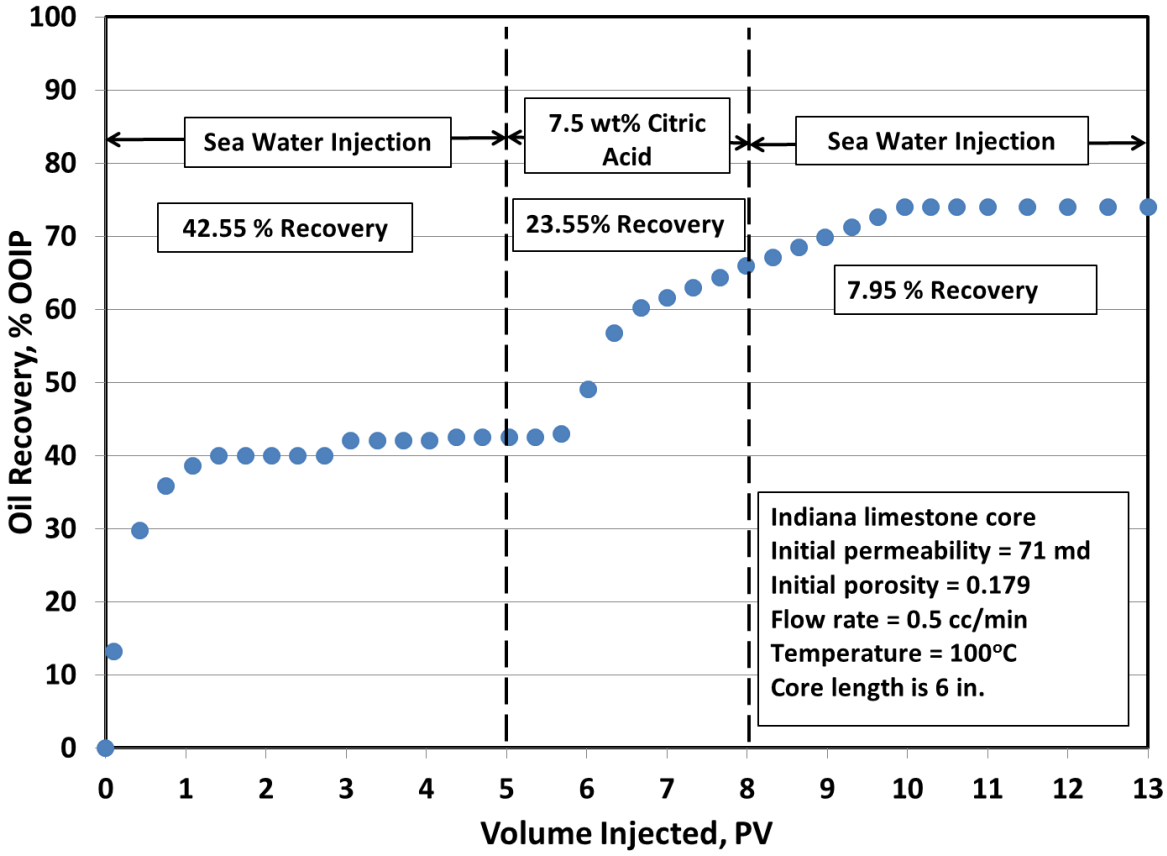


Figure 4-5 : Experiment#5. Citric Acid 7.5wt% (Recovery Factor vs PV Injected)

4.1.6 Experiment#6 (Encapsulated Citric acid 10wt %)

Following results were achieved with this test, as shown in Table 4-6 and Fig. 4-6. We injected 2 pore volume of sea water, which recovered 59% of OOIP. Initially core is completely saturated with oil and we get maximum amount of oil for the initial 0.75 pore volume of injection. Extra 1.25 pore volume of oil was injected to confirm that we cannot recover more from sea water injection. After this we shift the flow from sea water to 10 wt% encapsulated citric acid. During this flow we recover no additional oil as the capsule shells are required to be broken which is controlled by temperature. 2 pore volumes were injected to make sure encapsulated citric reaches every part of the core and then the flow is stopped and left at constant pressure mode of the equipment. Soaking time of 24 hours is given so that encapsulated shells are broken and citric acid reacts with carbonate to generate in-situ CO_2. Any extra pressure created due to CO_2 generation will be dealt by the system and constant pressure will be maintained inside the system. After 24 hours we again started flow shifting the system from constant pressure mode to constant flow rate. We get maximum oil recovery for the initial 1 pore volume of sea water injection and further 2 pore volume of oil were injected to make sure that maximum oil was recovered. We recovered 25% of OOIP from 3 pore volume of sea water injected.

We are able to report that the recoveries from each experiment with the difference of concentration are as follows. All results show that we recovered more oil for higher concentration of citric acid. The increase in recovery is summarized in table 4-7.

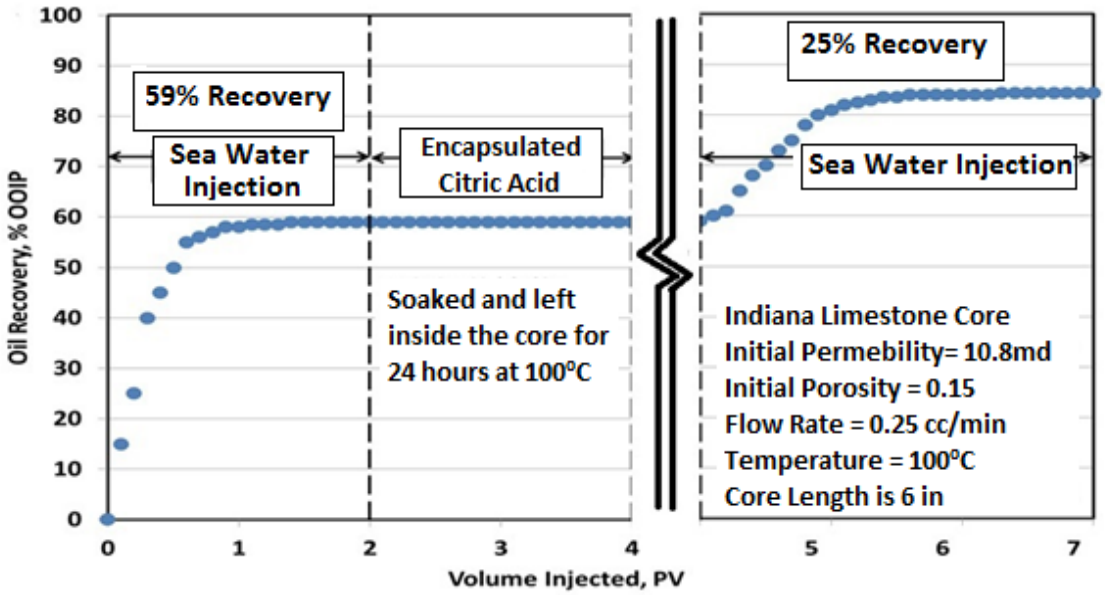


Figure 4-6 : Experiment#6. Encapsulated Citric acid 10wt % (Recovery Factor vs PV Injected)

Table 4-7 : Summary of Core Flooding Experiments and corresponding recoveries

Experiment #	Citric Acid wt%	Increased Recovery with Citric Acid Injection	Total Recovery Factor % of OOIP
1	2	11.6	61.5 (12 inch core was used instead of 6 inches)
2	5	9.02	52.5
3	7.5	31.5	74
4	10	42.5	83.8
5	Encapsulated Citric Acid 10wt %	25	84.3

Table 4-8: Sea water vs Spent Citric Acid

Experiment #	Injecting Fluid	Total Recovery Factor % of OOIP
1	Sea Water	41
2	10wt% Spent Citric Acid	49.3

4.2 Calculation of CO_2 Produced Using Simple Chemistry

Citric acid reacts with Calcium carbonate to evolve CO_2 in following proportions

$2C_6H_8O_7 + 3CaCO_3 = Ca_3(C_6H_5O_7)_2 + 3CO_2 + 3H_2O$

Citric acid + calcium carbonate = calcium citrate + Carbon dioxide+ water

2 moles of Citric acid produce = 3 moles of Carbon dioxide

1 moles of Citric acid produce = 1.5 moles of Carbon dioxide

X moles of Citric Acid Produce = X * 1.5 moles of Carbon dioxide

Now from these no of moles of CO_2 volume of CO_2 produced can be calculated as

Molar Volume = n * 22.4 Liter

1 Liter = 0.035 ft3

For SCF we can convert it by using

$$B_g = 0.0282 \frac{ZT}{P} \left(\frac{ft^3}{SCF}\right)$$

Suppose a volume of 5 ft3 is to be converted, at a pressure of 2000 psi and temperature of 100^{o}C, we will find as follows for CO_2

P_c=1071 psi

T_c= 67.91 F=572.91 R

T=100 ^{o}C= 212 F= 672 R

P=2000 psi

$T_r=T/T_c$= 672/572.91=1.17

$P_r=P/P_c$=2000/1071=1.86

z=0.55

$V_{sc}=V_r/B_g$= 5 /(0.0282*.55*672/2000)=5/0.0052=961.5 scf

4.3 Number of Moles of CO_2 Produced for One Pore Volume Citric Acid Injected

The length of core is 10 inch and diameter is 1.5 inch. And for a porosity value of 0.15, we can calculate the pore volume as follows

$$\text{Bulk Volume} = \pi r^2 l = 3.142 * \left(\frac{1.5}{2}\right)^2 (10) * (2.54)^3 = 289.62 \text{ cc}$$

$$\text{Pore Volume} = \Phi * \text{Bulk Volume} = 0.15 * 289.62 = 43.44 \text{ cc}$$

So 1 pore volume calculated is 43.44 cc, now we calculate moles of CO_2 produced

For 2 wt% of citric acid, 1 pore volume = 43.44 * 0.02 = 0.868 gram

As molecular weight of citric acid is 192, no of moles of citric acid will be

$$\text{no of moles of citric acid} = \frac{0.868}{192} = 0.0045 \text{ moles}$$

As described in the chemical equation

1 mole of citric acid produces = 1.5 moles of CO_2

0.0045*1 mole of citric acid produces = 1.5 * 0.0045 moles of CO_2

Number of moles of CO_2 produced will be 0.0068 moles.

4.4 IFT Measurements at High Temperature and Atmospheric Pressure

With the experiment performed, we are able to report the influence of citric acid solution in IFT reduction. As shown in table 4-9, IFT values for spent citric acid is lower than sea water at same PH=5, So this reduction will result in increased oil recovery . IFT values are low for higher concentration of spent citric acid. So higher concentration spent citric acid will result in more recovery compare to lower concentration.

Table 4-9: IFT Measurement at 100°C and atmospheric pressure

Solution	IFT measured with oil(30 °API) (m N/m)
Sea water diluted with HCL (PH=5)	20
2 wt% Spent Citric acid solution (PH=4.81)	8.73
5 wt% Spent Citric acid solution (PH=5)	6.5
10 wt% Spent Citric acid solution (PH=5)	4.75

4.5 Measurement of Interfacial Tension at HTHP using IFT700

IFT measurements conducted at high temperature and high pressure also resulted in similar IFT values trend. It can be seen that IFT values did not drop with increasing or decreasing pressure. But they depend on temperature. Higher concentration resulted in lower IFT values. This IFT reduction is the cause of extra oil recovery we discussed in core flooding experiment #4 with spent citric acid 10wt%.

4.5.1 IFT Results of Spent Citric Acid 10wt%

After running all IFT measurements following results were achieved with 10 wt% spent citric acid.

Table 4-10: At fixed Pressure of 2000 psi, IFT measurements of 10 wt % Spent Citric Acid with Oil at different temperature

Temperature (^{o}C)	IFT (mN/m)
30	11.78316
50	9.342941
70	9.026486
100	8.98873

Table 4-11: At fixed Temperature of 100 degree C, IFT measurements of 10wt % Spent Citric Acid with Oil at different Pressure

Pressure(Psi)	IFT (mN/m)
Atmospheric Pressure(pressure 16psi was able to be maintained)	11.35614
500	9.141931
1000	9.096116
1500	8.932927

4.5.2 IFT Results of Spent Citric Acid 5wt%

After running all IFT measurements following results were achieved with 5wt% spent citric acid.

Table 4-12: At fixed Pressure of 2000 psi, IFT measurements of 5wt % Spent Citric Acid with Oil at different temperature

Temperature (°C)	IFT (mN/m)
30	14.33759
50	14.16165
70	13.01517
100	11.12909

Table 4-13: At fixed Temperature of 100 degree C, IFT measurements of 5wt % Spent Citric Acid with Oil at different Pressure

Pressure(Psi)	IFT (mN/m)
Atmospheric Pressure(pressure 44psi was able to be maintained)	14.23228
500	11.21555
1000	11.22
1500	11.22869

4.6 CMG Simulations with reservoir at S_{or}

There are three different cases in which the simulation is divided in to this particular category

4.6.1 Inject CO_2 in to the reservoir and get recovery from it

Three well schemes are designed in this category

(i) Both injector and producer are horizontal(one injector and one producer well)

(ii) Both injectors and producers are vertical (Three vertical gas injectors and three vertical producers)

(iii) Vertical injectors and horizontal producers (Three vertical gas injectors and one horizontal producer)

The simulation time was decided from 2015 to 2034. In all scenarios maximum injector pressure is set to 5500 psi, and for producers maximum producing stock tank oil for a day is set to 30000bbl/day. No of wells and for each case are mentioned in the plots. The simulation was run with the decided design and following results were generated for oil average saturation (Fig. 4-7) and oil average recovery factor (Fig. 4-8).

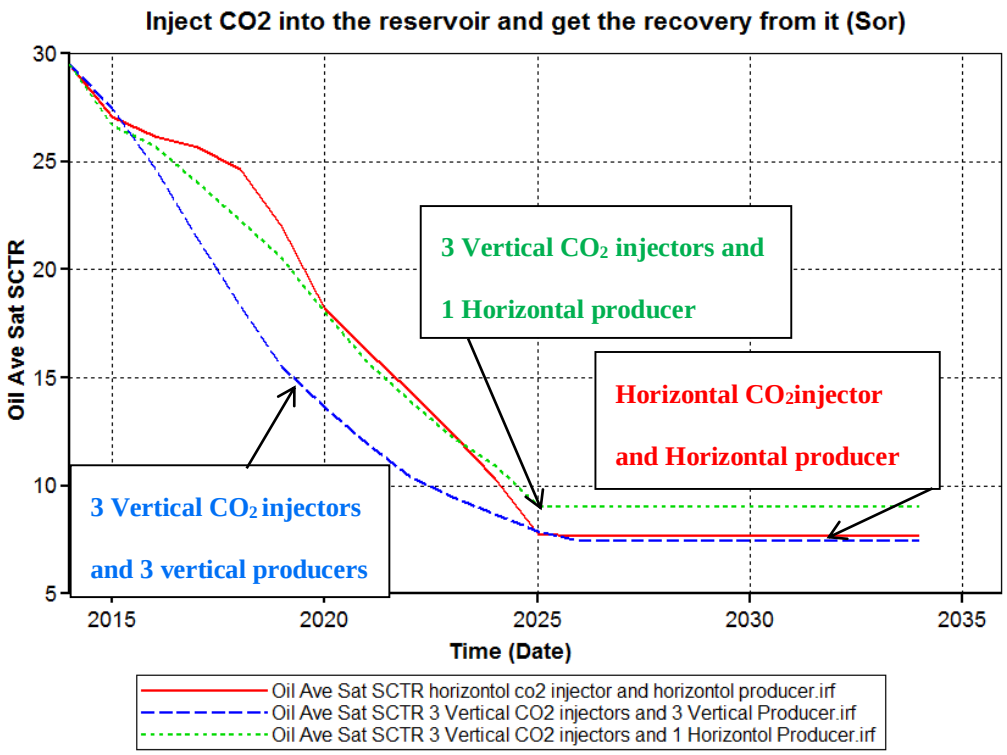


Figure 4-7 : Oil average saturation vs time (Inject CO_2 in to the reservoir and get recovery from it)

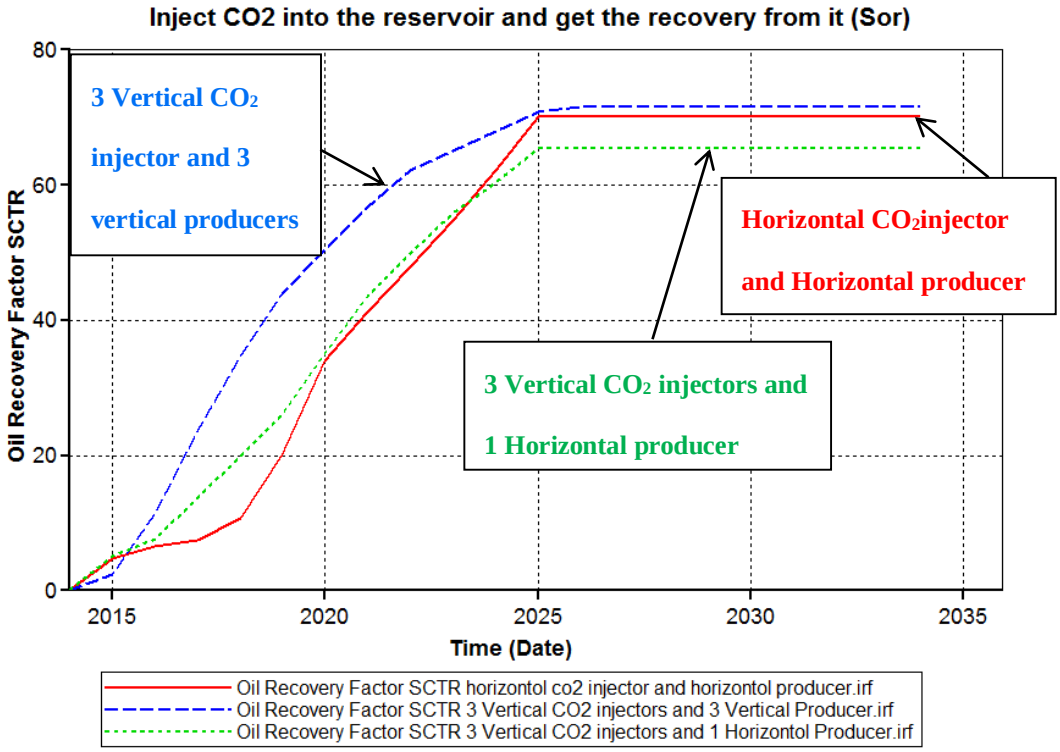


Figure 4-8 : Oil recovery factor vs time (Inject CO_2 in to the reservoir and get recovery from it)

4.6.2 Inject CO_2 in to the aquifer and produce naturally

Three well schemes are designed in this category

(i) Both injector and producer are horizontal(one injector and one producer well)

(ii) Both injectors and producers are vertical (Three vertical gas injectors and three vertical producers)

(iii) Vertical injectors and horizontal producers (Three vertical gas injectors and one horizontal producer)

The simulation time was decided from 2015 to 2034. In all scenarios maximum injector pressure is set to 5500 psi, and for producers maximum producing stock tank oil for a day is set to 30000bbl/day. No of wells and for each case are mentioned in the plots. The simulation was run with the decided design and following results were generated for oil average saturation (Fig. 4-9) and oil average recovery factor (Fig. 4-10).

In this case we inject CO_2 into the aquifer and produce. The vertical well scheme produces low at start but as the CO_2 saturation increases into the reservoir it makes more oil mobile and provide enough energy to reach production wells. This effect can also be seen in vertical injectors with horizontal producer case where production is high compare to horizontal injector but drops later when vertical injectors cannot provide more mobility to the oil as saturation of oil becomes as low as 13%. Vertical injector and producer with 3 wells each has better sweep and should be preferred.

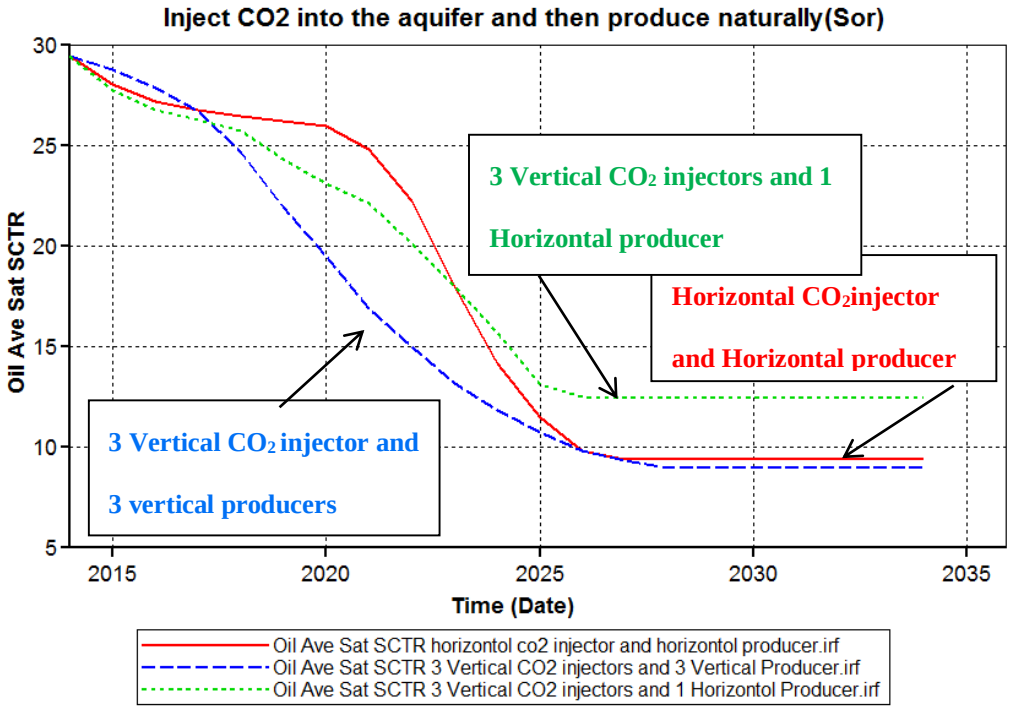


Figure 4-9: Oil average saturation vs time (Inject CO_2 in to the aquifer and produce naturally)

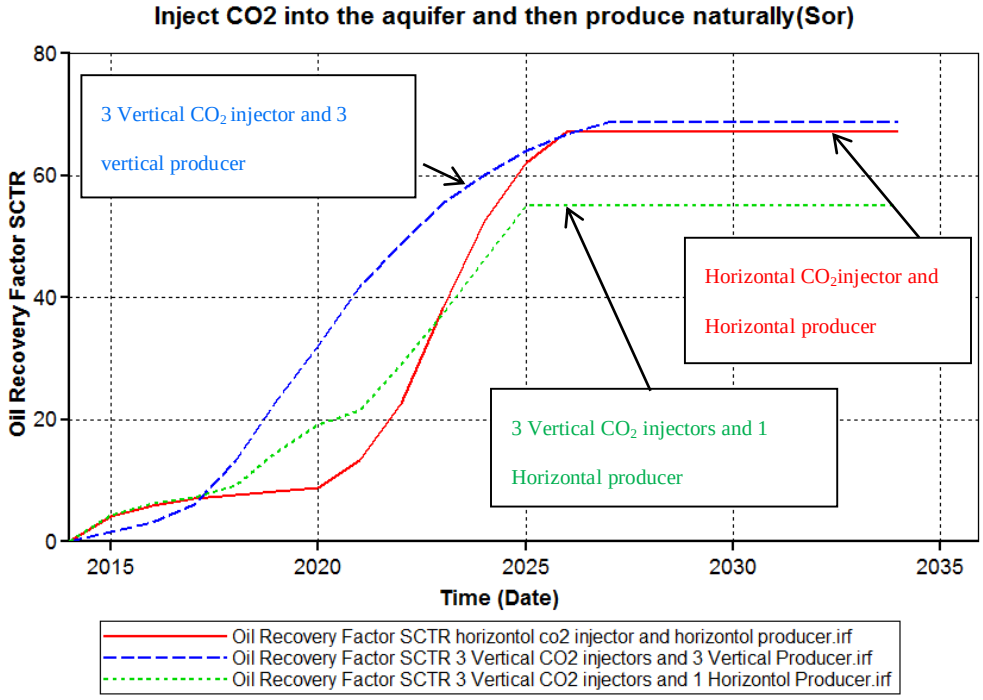


Figure 4-10: Oil recovery factor vs time (Inject CO_2 in to the aquifer and produce naturally)

4.6.3 Inject CO_2 in to the aquifer followed by water injection and get recovery

Three well schemes are designed in this category

(i) Both injector and producer are horizontal(One gas injectors, Two water injectors and one producer well)

(ii) Both injectors and producers are vertical (Three vertical gas injectors, Three vertical water injectors and Three vertical producers)

(iii) Vertical injectors and horizontal producers (Three vertical gas injectors, Three vertical water injectors and one horizontal producer)

The simulation time was decided from 2015 to 2034. In all scenarios maximum injector pressure is set to 5500 psi, and for producers maximum producing stock tank oil for a day is set to 30000bbl/day. No of wells and for each case are mentioned in the plots. The simulation was run with the decided design and following results were generated for oil average saturation (Fig. 4-11) and oil average recovery factor (Fig. 4-12).

In this case recovery drops to as low as 18%, with the maximum reaching 28% with the horizontal injector and horizontal producer. At start horizontal scheme works better but recovery becomes flat after 2023, this might be because of the pressure support was not there and when water reaches after CO_2 injection it recovers even more oil compare to other schemes.

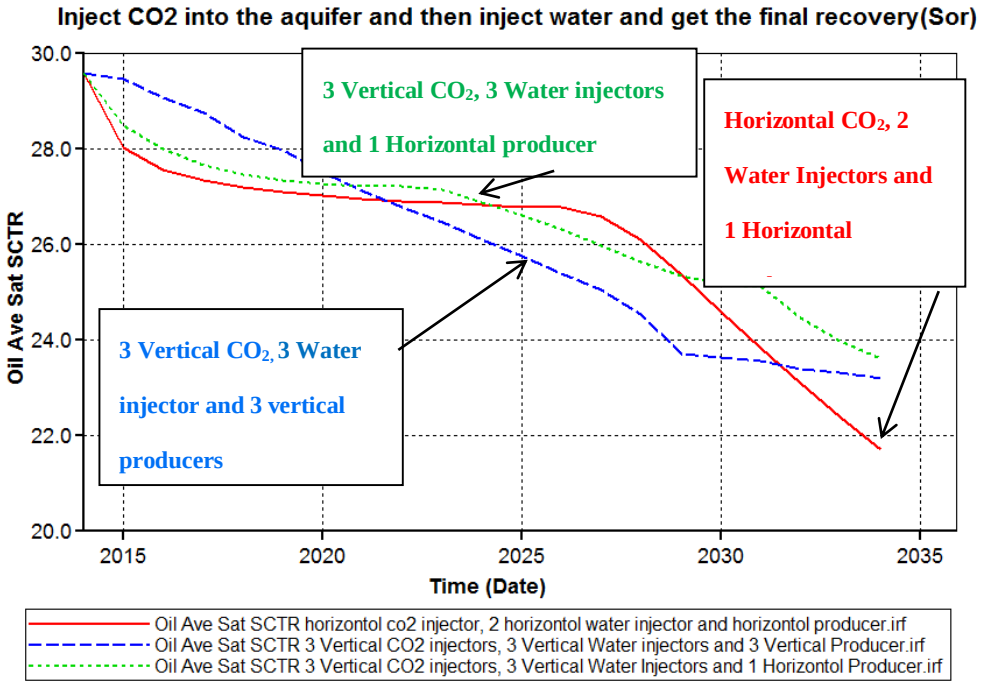


Figure 4-11: Oil average saturation vs time (Inject CO_2 in to the aquifer followed by water injection and get recovery)

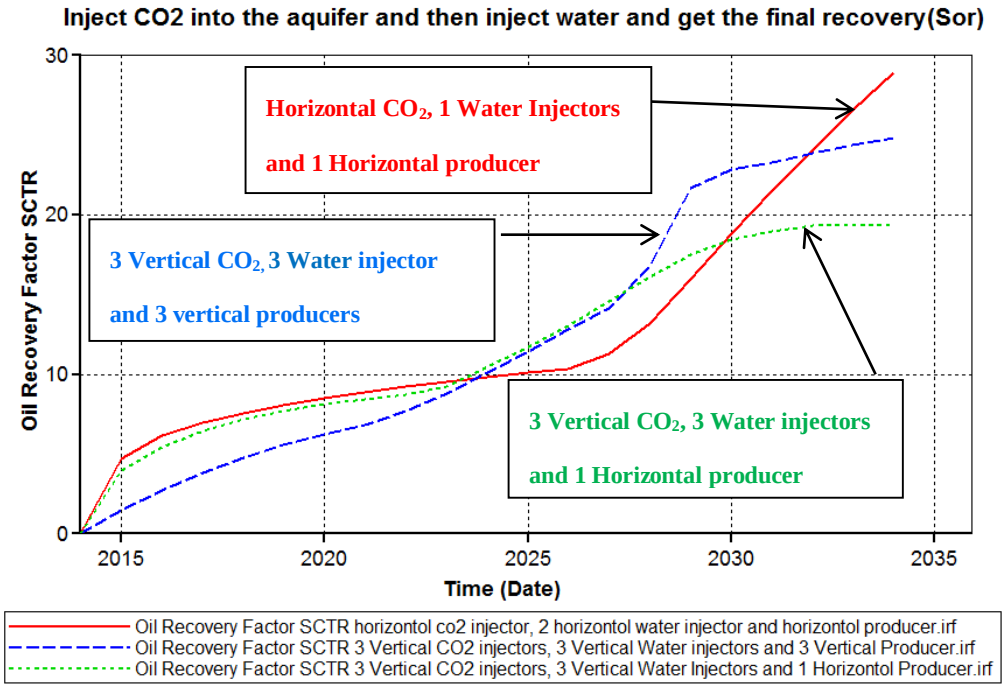


Figure 4-12: Oil recovery factor vs time (Inject CO_2 in to the aquifer followed by water injection and get recovery)

Table 4-14 summarizes the results of several cases of simulations in different conditions and different well schemes.

Table 4-14: For S_{or} case recoveries from different well schemes

Injection scheme adopted	% Recovery from horizontal injector and horizontal producer	% Recovery from vertical injectors and vertical producer	% Recovery from vertical injectors and horizontal producer
1) CO_2 injection into reservoir at S_{or}	71	73	66
2) CO_2 injection into aquifer at S_{or}	68	70	55
3) CO_2 injection into aquifer followed by water injection into aquifer	28	25	18

4.6.4 Inject CO_2 in to the aquifer and produce through it VS Sea water injection (Horizontal injector)

In case of in-situ generation of CO_2, CO_2 will release slowly to the oil and will react with it to reduce the oil viscosity. For this case we inject CO_2 directly in to the aquifer and it continues till the end and CO_2 injection is not stopped at any time. This is compared with only sea water injection; Fig. 4-13 compares the described case.

4.6.5 Inject CO_2 in to the aquifer followed by water injection VS Sea water injection (Horizontal injector)

We run other simulation in which we stop CO_2 flooding after maximum pressure of 3600psi was reached; Fig. 4-15. Average CO_2 saturation reached 10%; Fig.4-16. CO_2 flooding was stopped after year 2022 at this maximum pressure of 3600psi; Fig.4-17 and sea water flooding was continued till the end, after stopping CO_2 injection CO_2 fill up volume is generated due to which results in high pressure drop, a time gap is needed to fill this fill up volume and pressure rises; Fig.4-18 and we got increased oil recovery of 6.66% compare to only sea water injection; Fig. 4-14.

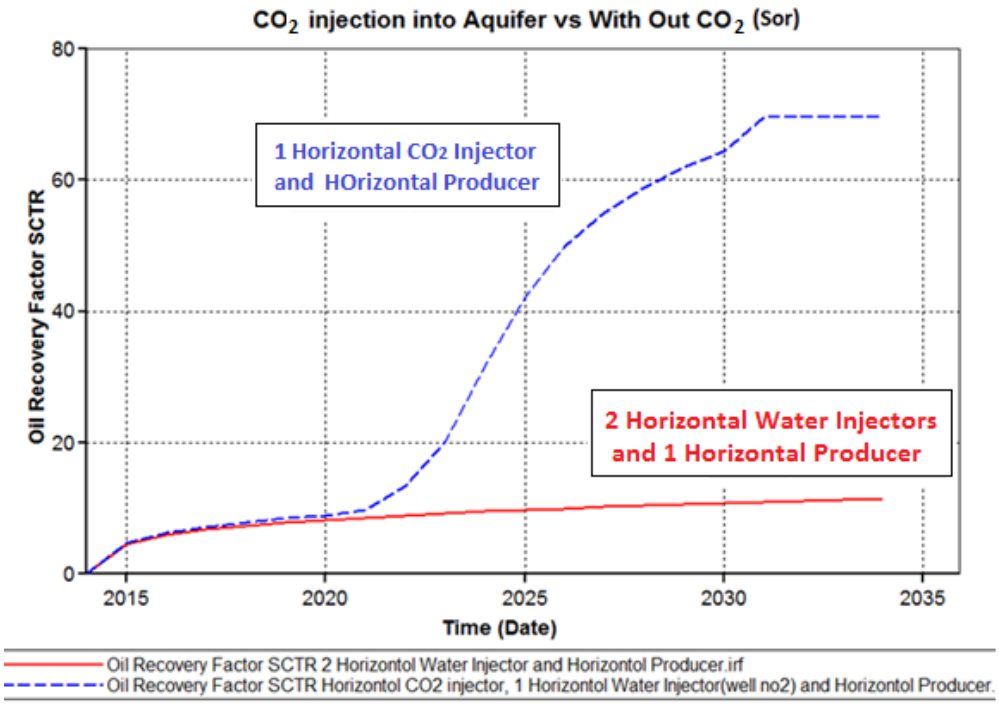


Figure 4-13: Oil Recovery Factor vs Time (CO_2 injection into the aquifer vs sea water horizontal injector)

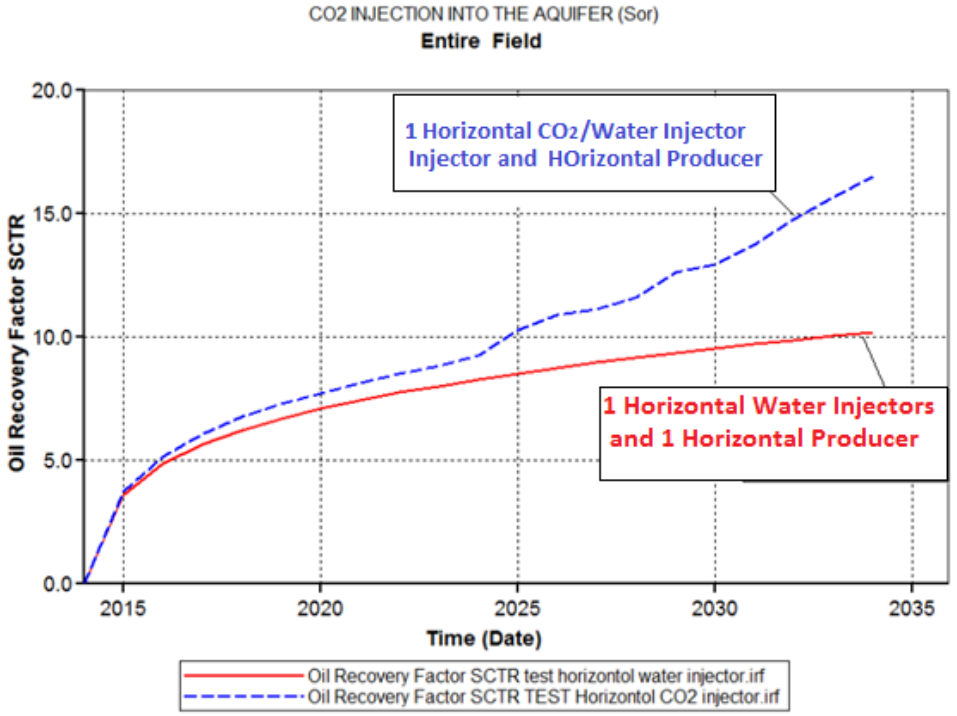


Figure 4-14: Oil Recovery Factor vs Time (CO_2 injection followed by water injection vs sea water injection only)

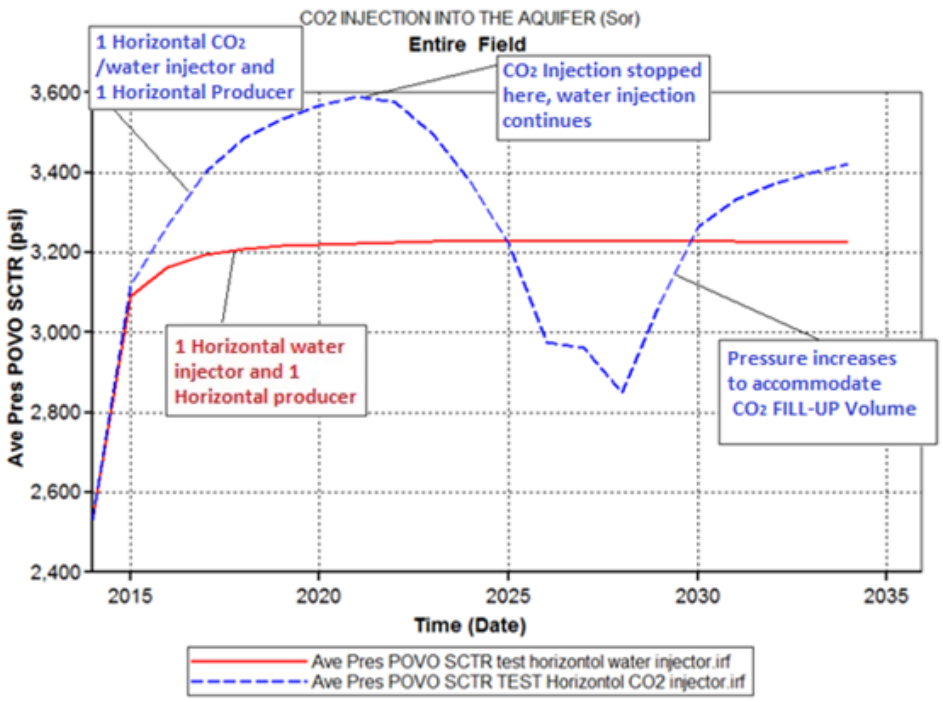


Figure 4-15: Average Reservoir Pore Volume Pressure vs Time (CO_2 injection followed by water injection vs sea water injection only)

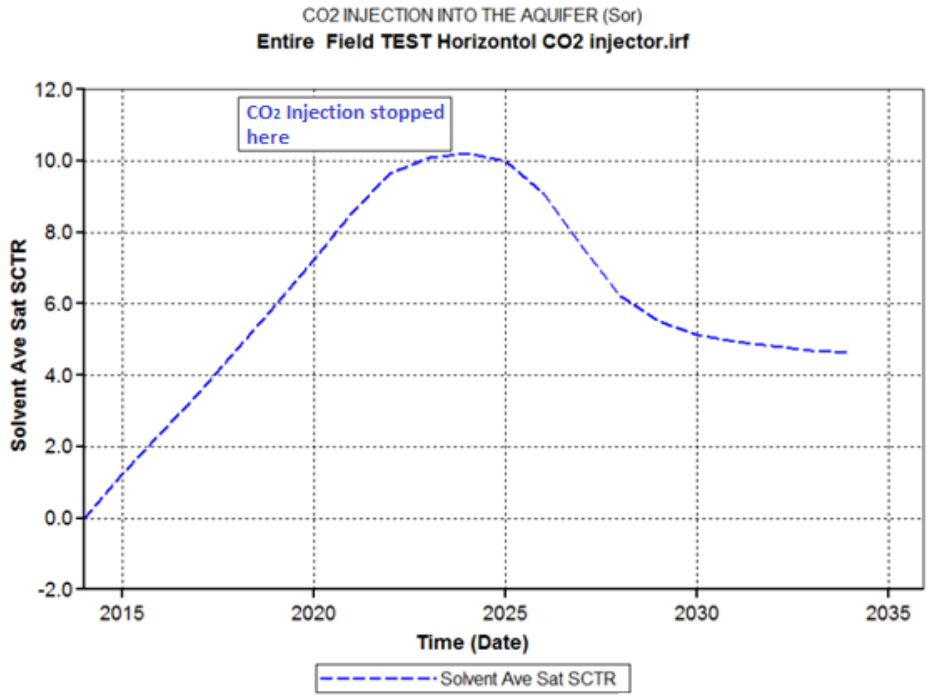


Figure 4-16 : CO_2 Solvent average saturation vs Time (CO_2 injection followed by water injection vs sea water injection only)

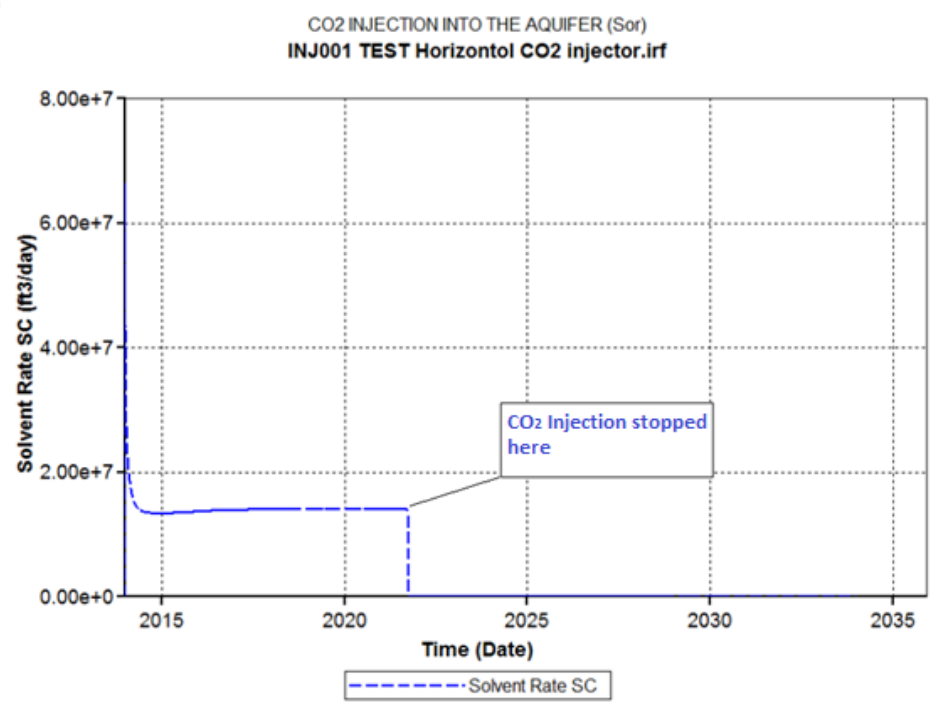


Figure 4-17: CO_2 Solvent Injection Rate vs Time (CO_2 injection followed by water injection vs sea water injection only)

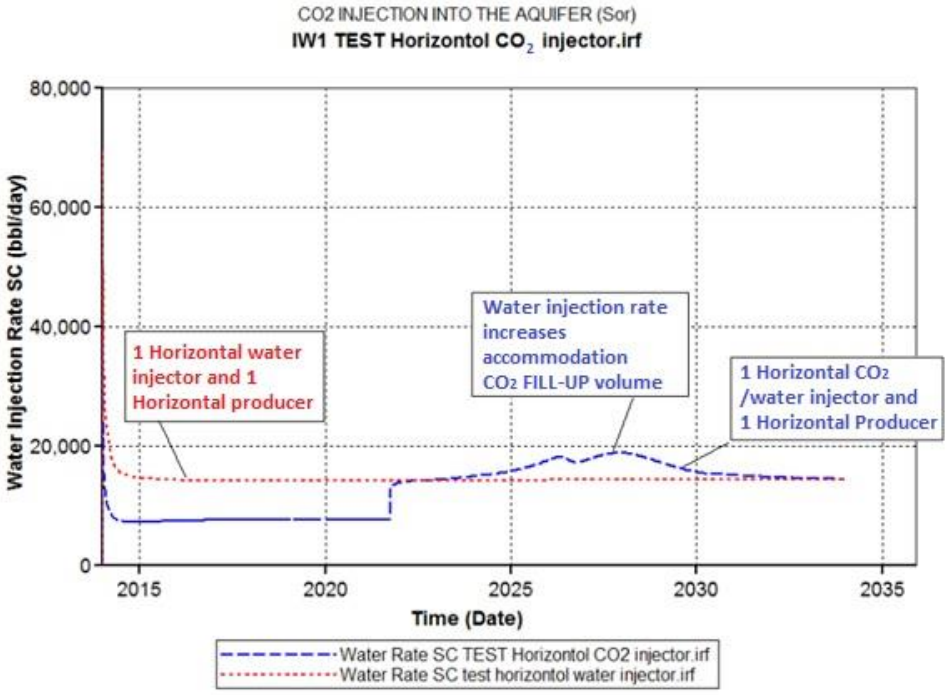


Figure 4-18: Water Injection Rate vs Time (CO_2 injection followed by water injection vs sea water injection only)

4.6.6 Inject CO_2 in to the aquifer followed by water injection VS Sea water injection (Vertical injector)

We run other simulation in which we stop CO_2 flooding after maximum pressure of 3700psi was reached; Fig. 4-20. Average CO_2 saturation reached 6%; Fig.4-21. CO_2 flooding was stopped after year 2019 at this maximum pressure of 3700psi; Fig.4-22 and sea water flooding was continued till the end, after stopping CO_2 injection CO_2 fill up volume is generated due to which results in high pressure drop (lesser compare to drop in horizontal injector case), we got increased oil recovery of 2.9% compare to only sea water injection; Fig. 4-19. We recovered lesser amount of recovery because in case of multiple vertical injector pressure rises sooner i.e. in this case 3 vertical injectors were used, and we got CO_2 saturation of 6% maximum, as a result less amount of oil was swelled and resulted in lesser recovery.

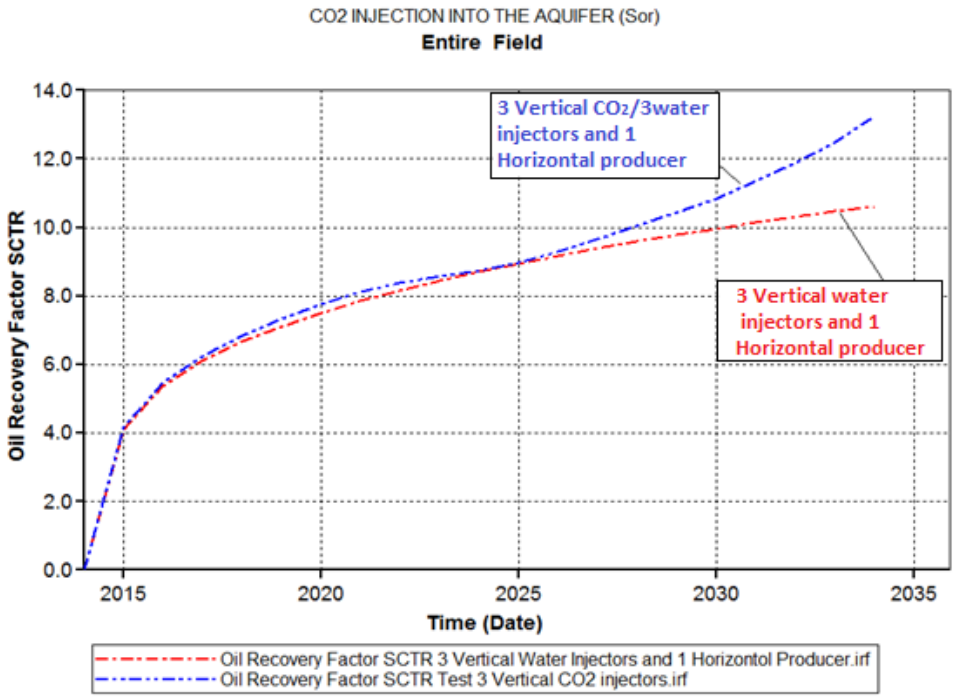


Figure 4-19: Oil Recovery Factor vs Time (CO_2 injection followed by water injection vs sea water injection only) Vertical Injector

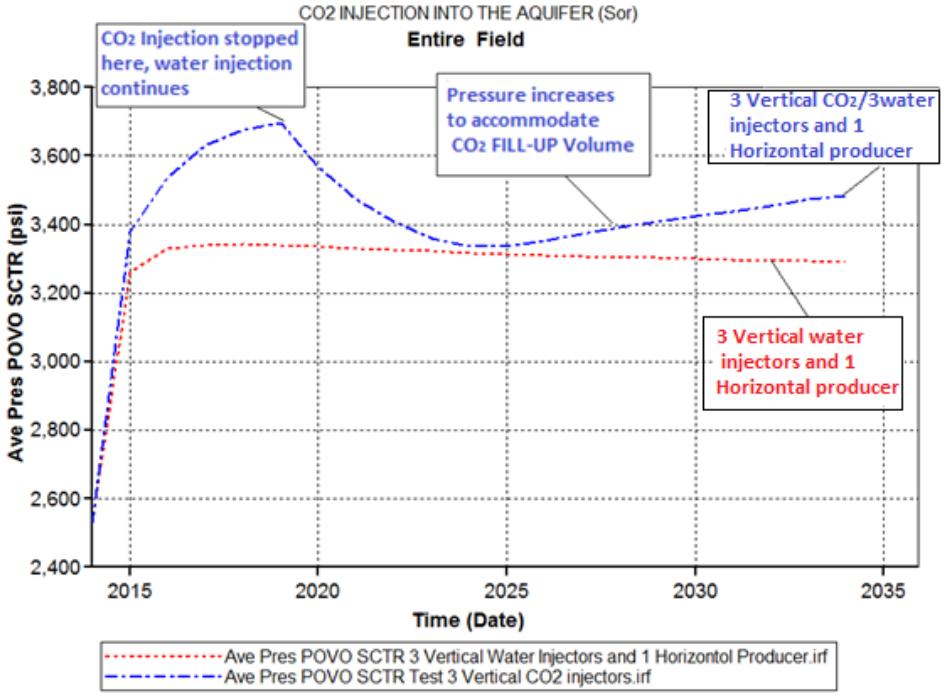


Figure 4-20: Average Reservoir Pore Volume Pressure vs Time (CO_2 injection followed by water injection vs sea water injection only) Vertical injector

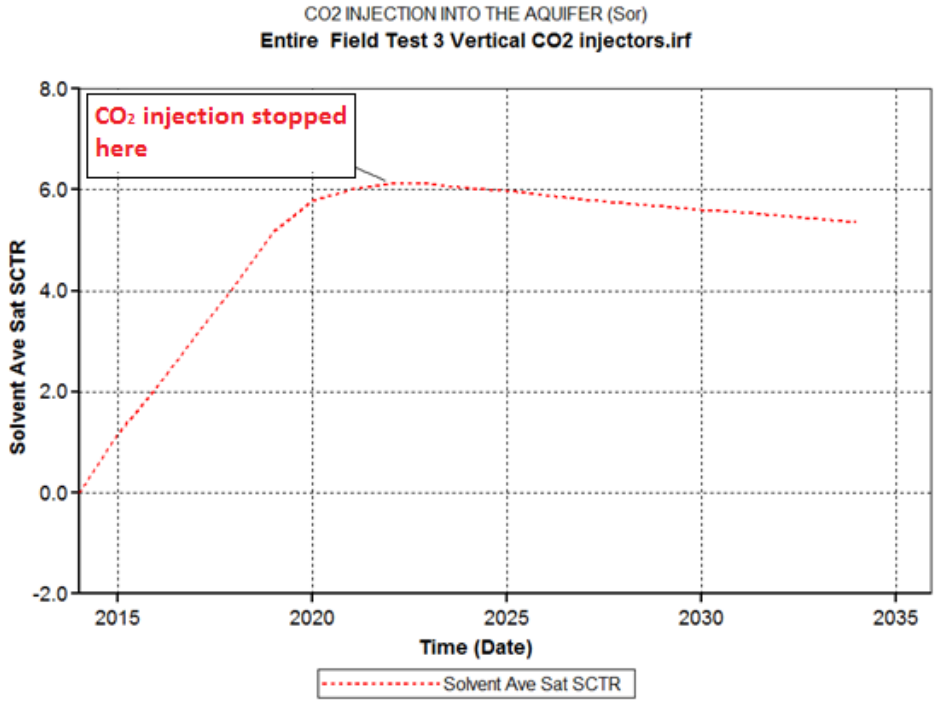


Figure 4-21 : CO_2 Solvent average saturation vs Time (CO_2 injection followed by water injection vs sea water injection only) Vertical injector

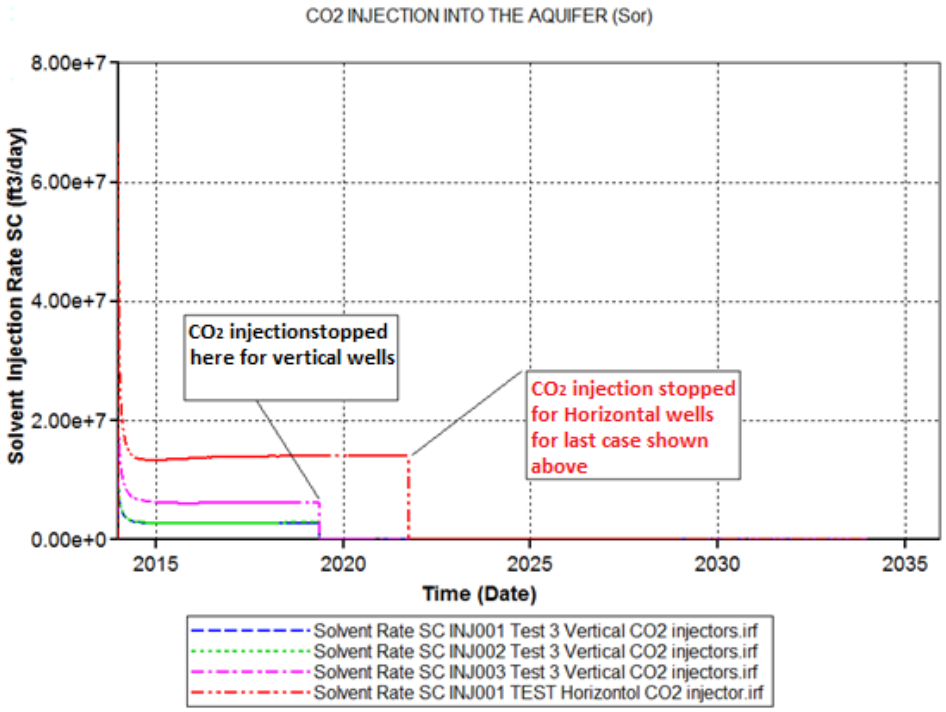


Figure 4-22 : Water Injection Rate vs Time (CO_2 injection followed by water injection vs sea water injection only)

Table 4-15 summaries the simulations ran to compare the CO_2 injection followed by water injection versus only sea water flooding.

Table 4-15: summary of the simulations with different well schemes

Well Scheme	% Recovery Sea water Injection	% Recovery CO_2 Injection followed by water injection
Horizontal injector and horizontal producers used	10.5	13.4
Vertical injector and horizontal producers used	10	16.66

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 On the basis of Experiments

On the basis of experiments performed we are able to conclude that in-situ CO_2 generation from citric acid generated good results. Oil recovery increased due to different concentrations of citric acid. Results suggest that in-situ generation of CO_2 can be adopted as one of favorable method for EOR.

On the basis of all the experiments performed and summary shown in table 4-7 it is clear that all the concentration of citric acid gave us some additional recovery in comparison to using only water flooding. As seen from results, 2% and 5wt% gave us low recovery and these concentrations gave us a maximum of 61.5% of OOIP. The lowest 2 wt% concentration has got more % recovery because in this experiment longer 12 inch core was used. As a result we saw recovery more than that of later 5wt% of citric acid. So we can conclude that it is because of the longer acid placement time. We can also achieve the same by injecting more pore volume of acid for shorter core to achieve the same results.

With further increase of concentration we get significant amount of recovery. The 7.5wt % resulted in 74% of OOIP and that of 10wt% resulted in 84% in both cases of encapsulated and non-encapsulated injection. So we can conclude that we get equal amount of recovery in both cases whether it is encapsulated acid or not. As explained in the experimental

procedure, after injection of 2 pore volume of encapsulated citric acid, 24 hours soaking time was given to make sure encapsulation shell is broken and CO_2 is generated and mixed with the oil to reduce its viscosity.

Experiment conducted with spent citric acid shown an additional 8% of OOIP that concludes that another mechanism of oil recovery in this process is formation of carboxylic acid group that is formed as bi-product (Calcium Citrate) is contributing for the additional recovery. So it can be concluded on the basis of experimental results that in-situ CO_2 is an effective method for increased oil recovery.

5.2 On the basis of CMG Simulations

In the first two cases it can be seen that vertical well injectors with vertical producers perform better in residual oil saturation. After that comes the vertical injectors case with horizontal producer, so we can conclude that in case of S_{or}, vertical injectors perform better along with or with vertical producers and even shows benefit of vertical injectors in case of its use with horizontal producers.

Injection of CO_2 into the aquifer till the end resulted in 70% increased recovery compare to sea water flooding recovery of 10%. This confirms that CO_2 is mixing with the remaining oil and can produce maximum amount of oil if we allow more CO_2 to rise to the upper reservoir layer. Increased recovery is directly related to the amount of CO_2 injected. Injecting CO_2 into the aquifer resulted in very low recovery as low as 18% from vertical injectors and horizontal producer case.

So these initial tests with CMG simulation suggest that it validates the CO_2 slow release concept to the reservoir. And we got increased recovery of 6.66% in the case of horizontal injectors and 2.9% in the case of vertical injectors compare to that of sea water only.

5.3 Recommendations

We further recommend that

- An extensive kinetics study should be carried out to account for the dissolution of rock beside other mechanisms studied in this research.
- CMG Simulation Work can be extended for different scenarios/well locations to achieve Optimum results.

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Appendices

Table 4-1: Experiment # 1 Citric acid 2wt % (Recovery Factor vs PV Injected)

Pore Volume Injected	Recovery Factor
0	0
0.051993	2.360248
0.225303	27.20497
0.398614	37.76398
0.571924	39.00621
0.745234	40.62112
0.918544	42.1118
1.091854	43.35404
1.265165	44.7205
1.438475	44.7205
1.611785	44.7205
1.785095	44.74534
1.958406	44.79503
2.131716	45.54037
2.305026	45.54037
2.478336	46.78261
2.651646	46.78261
2.824957	46.78261

2.998267	46.78261
3.171577	46.78261
3.344887	46.78261
3.518198	46.78261
3.691508	47.52795
3.864818	47.52795
4.038128	47.7764
4.211438	47.7764
4.384749	47.7764
4.558059	48.27329
4.731369	48.27329
4.904679	48.27329
4.904679	48.27329
5.07799	48.52174
5.2513	48.52174
5.42461	48.52174
5.59792	48.52174
5.771231	48.52174
5.944541	48.64596
6.117851	48.64596
6.291161	48.64596

6.291161	48.64596
6.464471	48.77019
6.637782	49.01863
6.811092	49.3913
6.984402	49.63975
7.157712	49.8882
7.331023	49.8882
7.504333	49.8882
7.677643	49.8882
7.850953	49.8882
8.024263	49.8882
8.197574	49.8882
8.370884	49.8882
8.544194	49.8882
8.717504	50.33988
8.890815	50.79155
9.064125	51.24323
9.237435	51.69491
9.410745	52.14658
9.584055	52.59826
9.757366	53.04994

9.930676	53.50161
10.10399	53.95329
10.2773	54.40497
10.45061	54.85665
10.62392	55.30832
10.79723	55.76
10.97054	56.21168
11.14385	56.66335
11.31716	57.11503
11.49047	57.56671
11.66378	58.01839
11.83709	58.47006
12.0104	58.92174
12.18371	59.37342
12.35702	59.82509

Table 4-2 : Experiment # 2 Citric acid 10wt % (Recovery Factor vs PV Injected)

Pore Volume Injected	Recovery Factor
0	0
0.102916	5.238095
0.445969	34.52381
0.789022	36.42857
1.132075	37.14286
1.475129	37.85714
1.818182	38.09524
2.161235	38.09524
2.504288	38.09524
2.847341	39.04762
3.190395	39.52381
3.533448	39.7619
3.876501	41.19048
4.219554	41.19048
4.562607	41.19048
4.90566	41.28571
4.90566	41.28571
5.248714	41.90476

5.591767	42.28571
5.93482	42.90476
6.277873	46.38095
6.620926	50.33333
6.963979	55
7.307033	61.33333
7.650086	65.04762
7.993139	69.2381
8.336192	75.57143
8.336192	75.95238
8.679245	80.14286
9.022298	81.47619
9.365352	82.33333
9.708405	83.19048
10.05146	83.80952

Table 4-3 : Experiment # 3 Citric acid 5wt % (Recovery Factor vs PV Injected)

Pore Volume Injected	Recovery Factor
0	0
0.102569	16.16628
0.444464	33.25635
0.78636	37.87529
1.128255	38.10624
1.470151	39.03002
1.812046	39.49192
2.153942	40.8776
2.495837	41.10855
2.837733	42.72517
3.179628	42.95612
3.521524	43.18707
3.86342	43.18707
4.205315	43.18707
4.547211	43.18707
4.889106	43.41801
4.889106	43.41801
5.231002	43.64896

5.572897	44.11085
5.914793	44.57275
6.256688	44.8037
6.598584	45.72748
6.940479	46.42032
7.282375	46.88222
7.62427	47.11316
7.966166	47.34411
8.308062	47.34411
8.308062	47.34411
8.649957	48.12933
8.991853	49.83834
9.333748	50.8545
9.675644	51.63972
10.01754	52.42494

Table 4-4 : Experiment # 4 Spent Citric acid 10wt % (Recovery Factor vs PV Injected)

Pore Volume Injected	Recovery Factor
0	0
0.087984	18.03662
0.381265	32.95214
0.674546	36.83978
0.967827	40.51935
1.261108	42.11819
1.554389	43.0928
1.84767	43.85934
2.140951	44.41781
2.434232	44.97628
2.727513	45.53475
3.020794	46.09322
3.314075	46.65169
3.607355	47.21015
3.900636	47.56055
4.193917	47.91094
4.487198	48.26134
4.780479	48.61174

5.07376	48.96213
5.367041	49.31253

Table 4-5 : Experiment # 5 Citric acid 7.5wt % (Recovery Factor vs PV Injected)

Pore Volume Injected	Recovery Factor
0	0
0.098636	13.25581
0.427421	29.76744
0.756206	35.81395
1.084991	38.60465
1.413776	40
1.742561	40
2.071346	40
2.400132	40
2.728917	40
3.057702	42.09302
3.386487	42.09302
3.715272	42.09302
4.044057	42.09302
4.372842	42.55814
4.701627	42.55814
5.030413	42.55814
5.359198	42.55814

5.687983	42.55814
6.016768	42.55814
6.345553	43.02326
6.674338	49.06977
7.003123	56.74419
7.331909	60.23256
7.660694	61.60465
7.989479	62.97674
8.318264	64.34884
8.318264	64.34884
8.647049	65.72093
8.975834	67.09302
9.304619	68.46512
9.633405	69.83721
9.96219	71.2093
10.29097	72.5814
10.61976	73.95349

Table 4-6 : Experiment # 6 Encapsulated Citric acid 10wt % (Recovery Factor vs PV Injected)

Pore Volume Injected	Recovery Factor
0	0
0.1	15
0.2	25
0.3	40
0.4	45
0.5	50
0.6	55
0.7	56
0.8	57
0.9	58
1	58
1.1	58.5
1.2	58.5
1.3	58.5
1.4	59
1.5	59
1.6	59
1.7	59

1.8	59
1.9	59
2	59
2.1	59
2.2	59
2.3	59
2.4	59
2.5	59
2.6	59
2.7	59
2.8	59
2.9	59
3	59
3.1	59
3.2	59
3.3	59
3.4	59
3.5	59
3.6	59
3.7	59
3.8	59

3.9	59
4	59
4.1	60
4.2	61
4.3	65
4.4	68
4.5	70
4.6	73
4.7	75
4.8	78
4.9	80
5	81
5.1	82
5.2	82.5
5.3	83
5.4	83.5
5.5	83.5
5.6	84
5.7	84
5.8	84
5.9	84

6	84
6.1	84
6.2	84
6.3	84.3
6.4	84.3
6.5	84.3
6.6	84.3
6.7	84.3
6.8	84.3
6.9	84.3
7	84.3

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